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(54) ELECTRODE CATALYST LAYER, FILM-ELECTRODE COMPLEX AND THEIR MANUFACTURING METHOD AND BATTERY USING SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thin electrode catalyst layer with high catalyst utilization efficiency and high output performance by restraining deterioration of performance due to coating defect in forming an electrode catalyst layer and a cost hike due to complicated processes.

SOLUTION: The electrode catalyst layer has a catalyst-polymer complex composed of at least a catalyst layer and a polymer integrally constructed with a holding layer composed of a porous conductive sheet and/or non-conductive cloth, with thickness of 50  $\mu$ m or less.

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**CLAIMS**


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## [Claim(s)]

[Claim 1] The electrode catalyst bed whose thickness it has the structure with which an electrode catalyst, the catalyst-polymer complex which consists of polymers, and \*\*\*\*\* which comes to have a porosity electric conduction sheet and/or a non-conductive textile were united at least, and is 50 micrometers or less.

[Claim 2] The electrode catalyst bed according to claim 1 whose porosity electric conduction sheet is the thing of the textile-fabrics structure using inorganic conductivity fiber, or non-woven fabric structure.

[Claim 3] The electrode catalyst bed according to claim 1 whose non-conductive textile is the thing of the textile-fabrics structure using fiber, or non-woven fabric structure.

[Claim 4] The electrode catalyst bed according to claim 2 whose inorganic conductivity fiber is a carbon fiber.

[Claim 5] The electrode catalyst bed according to claim 3 which is fiber for which the fiber of a non-conductive textile comes to contain a fluorine atom.

[Claim 6] The electrode catalyst bed according to claim 1 to 5 by which it comes to fill up catalyst-polymer complex all over the opening of \*\*\*\*\*.

[Claim 7] The electrode catalyst bed according to claim 1 to 6 which is the sheet with which the gestalt of an electrode catalyst bed can become independent.

[Claim 8] The electrode catalyst bed containing the element more than a kind chosen from the group which an electrode catalyst becomes from platinum, palladium, gold, a ruthenium, and iridium according to claim 1 to 7.

[Claim 9] The electrode catalyst bed according to claim 1 to 8 which is carbon black with which the electrode catalyst supported the catalyst.

[Claim 10] The electrode catalyst bed according to claim 1 to 9 which is the polymer in which a polymer contains a fluorine atom.

[Claim 11] The electrode catalyst bed according to claim 1 to 10 which is the polymer in which a polymer has a proton exchange group.

[Claim 12] The manufacture approach of the electrode catalyst bed according to claim 1 to 11 characterized for the liquid containing catalyst-polymer complex or its precursor by to sink in or carrying out coating at a porosity electric conduction sheet or a non-conductive textile.

[Claim 13] Film-electrode complex which consists of an electrode catalyst bed according to claim 1 to 11, and the proton exchange film and an electrode substrate.

[Claim 14] Film-electrode complex according to claim 13 with which the proton exchange film comes to have a fluorine atom content polymer.

[Claim 15] Film-electrode complex according to claim 14 which is the polymer which comes to have the fluoro alkyl ether side chain with which a fluorine atom content polymer has a sulfonic group, and a fluoro alkyl principal chain.

[Claim 16] Film-electrode complex according to claim 13 to 15 whose electrode substrate is a porosity electric conduction sheet.

[Claim 17] Film-electrode complex according to claim 16 whose porosity electric conduction sheet is the textile-fabrics structure or non-woven fabric structure using inorganic conductivity fiber.

[Claim 18] Film-electrode complex according to claim 17 whose inorganic conductivity fiber is a carbon fiber.

[Claim 19] The manufacture approach of the film-electrode complex characterized by arranging the proton exchange film between two electrode catalyst beds according to claim 1 to 11, making the electrode

catalyst bed which pinched said proton exchange film pinch between two electrode substrates, and joining.

[Claim 20] Electrochemistry equipment using an electrode catalyst bed according to claim 1 to 11.

[Claim 21] Electrochemistry equipment using film-electrode complex according to claim 13 to 18.

[Claim 22] Water electrolysis equipment using an electrode catalyst bed according to claim 1 to 11.

[Claim 23] Water electrolysis equipment using film-electrode complex according to claim 13 to 18.

[Claim 24] The fuel cell using an electrode catalyst bed according to claim 1 to 11.

[Claim 25] The fuel cell using film-electrode complex according to claim 13 to 18.

[Claim 26] The fuel cell according to claim 24 or 25 using a solid-state macromolecule mold electrolyte.

[Claim 27] The mobile which makes a fuel cell according to claim 24 or 25 a power source of supply.

[Claim 28] The automobile which makes a fuel cell according to claim 24 or 25 a power source of supply.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the electrodes or film-electrode complex which are used for a fuel cell or various electrochemistry equipments, and those manufacture approaches.

[0002]

[Description of the Prior Art] A fuel cell is the low power plant of the burden to an environment at low excretions and high energy effectiveness. For this reason, it is in the limelight again in the rise to earth environmental protection in recent years. Compared with the conventional large-scale generation-of-electrical-energy facility, it is the power plant expected also in the future as power plants of a mobile, such as a comparatively small-scale distributed generation-of-electrical-energy facility, an automobile, and a marine vessel.

[0003] There is a class of a solid-state macromolecule mold, a phosphoric-acid mold, a solid acid ghost mold, a melting carbonate mold, alkali mold, etc. of fuel cells according to the class of electrolyte used. Especially, compared with other fuel cells, warm-up time of an operating temperature is short at low temperature, and a polymer electrolyte fuel cell has the descriptions which high power tends to acquire, like that it can count upon small lightweight-ization, and it is strong to an oscillation, and fits the power supply source of a mobile.

[0004] The fuel cell is constituted considering the cel into which the electrolyte used as the anode with which the reaction which bears a generation of electrical energy occurs, the electrode of a cathode, and an anode and the ion conductor between cathodes was inserted with the separator between each as a unit. The electrode consists of acceleration of gaseous diffusion, an electrode substrate (it is also called a charge collector) which performs \*\* (\*\*) \*\*, and an electrode catalyst bed which serves as an electrochemical reaction field actually. For example, in the anode electrode of a polymer electrolyte fuel cell, fuel gas reacts on a catalyst front face, a proton and an electron are produced, an electron is conducted to an electrode substrate, and a proton is conducted to the electrolytic proton exchange film. For this reason, it is required for an anode electrode that gaseous diffusion nature, electronic conductivity, and ionic conduction nature should be good. On the other hand, in a cathode electrode, the proton which oxidation gas has conducted from the electrolyte on the catalyst bed front face, and the electron conducted from the electrode substrate react, and water is generated. For this reason, it is also necessary to discharge efficiently the water generated with gaseous diffusion nature, electronic conductivity, and ionic conduction nature.

[0005] From such a point, in the electrode substrate (charge collector), it had conductivity, and the good porosity electric conduction sheet of gas permeability has been used. Although gas permeability was good, when such a porosity electric conduction sheet carried out coating of the electrode catalyst bed on the sheet, the phenomenon in which the catalyst coating liquid into a hole permeated was seen. Since proton conductivity falls since the catalyst which permeated has distance with the proton exchange film, and the thickness of a catalyst bed becomes thick, the diffusibility of gas serves as a defect. For this reason, the catalyst which is not used effectively will increase according to this catalyst \*\*\*\* lump phenomenon. Since the catalyst of noble metals is used in a fuel cell, that the catalyst which is not used effectively increases leads to the cost rise of an electrode. Especially a polymer electrolyte fuel cell has the high expectation for an automotive application. Cost also serves as an important factor with the engine performance at adaptation in an automotive application. If low cost-ization is made, as for the current polymer electrolyte fuel cell, much more spread is expected.

[0006] For this reason, the electrode with few catalyst \*\*\*\* lumps is called for, and various proposals were

made. For example, JP,10-261,001,A, WO 98/27606, JP,7-78617,A, and \*\*\*\* No. 501541 [ nine to ] official report, JP,10-92439,A, JP,10-92440,A, etc. are indicated as a well-known example, such as filling up the opening of a porous electrode substrate with a carbon particle, and preparing a catalyst \*\*\*\* lump control layer in an electrode substrate front face.

[0007] Moreover, they are J.Electrochem.Soc., 139, L28 (1992), and Electrochimica as a well-known example of imprinting on the film, after applying to the coating base material which prepares an electrode catalyst bed on the proton exchange film, without applying to a porous electrode substrate. Acta, 40,355 (1995), J.Appl.Electrochem., 22, 1 (1992), etc. are indicated.

[0008]

[Problem(s) to be Solved by the Invention] In the above-mentioned proposal, although the permeate lump of the catalyst bed to an electrode substrate was controlled, it had had the adverse effect on the fuel cell engine performance. In approaches, such as filling up the opening of a porous electrode substrate with a carbon particle, and preparing a catalyst \*\*\*\* lump control layer in an electrode substrate front face, gaseous diffusion nature, such as a steam for hydrogen, air, or humidification, will be checked, buildup of diffusion polarization or activation polarization will be caused, and loss of power will be caused.

[0009] Moreover, in the approach of imprinting on the film, after preparing or applying an electrode catalyst bed to a coating base material on the proton exchange film, without applying to a porous electrode substrate, the special process was needed in order to suppress swelling of the proton exchange film by catalyst coating liquid, it has a complicated process and there was a problem that cost started.

[0010] The above-mentioned technical problem is solved, the high power engine performance is discovered, and the utilization effectiveness of this invention of a catalyst improves, and it aims at the low cost-ized electrode by the amount reduction of catalysts being obtained.

[0011]

[Means for Solving the Problem] In this invention, in order to solve the above-mentioned technical problem, it has the following configuration.

[0012] That is, the electrode catalyst bed of this invention has the structure with which an electrode catalyst, the catalyst-polymer complex which consists of polymers, and \*\*\*\*\* which comes to have a porosity electric conduction sheet and/or a non-conductive textile were united at least, and is characterized by thickness being 50 micrometers or less.

[0013]

[Embodiment of the Invention] Hereafter, the gestalt of desirable operation of this invention is explained.

[0014] This invention has the structure with which \*\*\*\*\* (only henceforth "\*\*\*\*\*") which consists of an electrode catalyst, the catalyst-polymer complex which consists of polymers, a porosity electric conduction sheet, and/or a non-conductive textile at least was united, and is characterized by thickness being 50 micrometers or less, and \*\*\*\*\* and the electrode catalyst which are used here, especially a polymer, etc. are not limited.

[0015] In this invention, it is the description to have the structure with which catalyst-polymer complex and \*\*\*\*\* were united. The united structure as used in the field of here has pointed out the condition that catalyst-polymer complex exists in the front face or the opening inner surface of \*\*\*\*\* or the condition of filling up with catalyst-polymer complex all over the opening of \*\*\*\*\* , and the condition that catalyst-polymer complex has covered \*\*\*\*\* . Moreover, the need of existing in homogeneity at the whole \*\*\*\*\* does not have catalyst-polymer complex in the thickness direction, and where one side is approached, you may exist. However, existing in homogeneity is desirable in the direction vertical to the thickness direction of a field, i.e., the direction.

[0016] When the porosity conductive liner sheet of \*\*\*\*\* consists of inorganic conductivity fiber like the after-mentioned, the condition that catalyst-polymer complex exists in the clearance between fiber and fiber, the condition which exists in the surroundings of fiber, the condition of existing in the confounding point of fiber and fiber, etc. are the united structures.

[0017] The electrode catalyst bed of this invention differs from the case (that is, the condition from which are independently separated of \*\*\*\*\* and catalyst-polymer complex, the condition that the layer of catalyst-polymer complex can be divided from \*\*\*\*\* ) where catalyst-polymer complex and \*\*\*\*\* are not one. Since it is the same as the gestalt of the film-electrode complex (MEA) which will be in the condition which prepared the electrode catalyst bed on the electrode substrate which consists of a porosity electric conduction sheet when it was not one, or the condition of having joined the proton exchange film which prepared the electrode catalyst bed to the electrode substrate which consists of a porosity electric conduction sheet, and consists of the conventional electrode substrate-electrode catalyst bed-proton exchange film, it differs from the embodiment of this invention.

[0018] In this invention, it is the description that the thickness of an electrode catalyst bed is 50 micrometers or less, and the electrode catalyst beds with which a 100–300 micrometer electrode substrate and catalyst–polymer complex were united in the conventional phosphoric acid fuel cell differ fundamentally. Although a polymer electrolyte fuel cell requires that it should be the description that high power is obtained and for that it should make internal resistance of a fuel cell low, it is also important to suppress lowering of the electrical potential difference by the activation polarization in a low current region and lowering of the electrical potential difference by diffusion polarization in a high current region. The one where the thickness of an electrode catalyst bed is thinner is desirable also for suppressing which polarization, and it is needed for it from this point that the thickness of the electrode catalyst bed of this invention is 50 micrometers or less. 30 micrometers or less are 20 micrometers or less more preferably. However, the thing a press performs [ thing ] thin film–ization for a non–conductive textile like the after–mentioned, Or since some press processes are performed, pressing, after unifying catalyst–polymer complex and a non–conductive textile, pressing an electrode substrate, an electrode catalyst bed, and the proton exchange film in film–electrode complex creation time further, etc. It becomes the description of this invention that the thickness of the electrode catalyst bed when being used eventually is 50 micrometers or less.

[0019] In this invention, the thickness of an electrode catalyst bed can be checked by scanning electron microscope (SEM) observation of an electrode cross section. When it is a metaled electrode catalyst, an electrode catalyst bed is using together SEM and X–ray microanalysis (XMA) (SEM–XMA), and can be asked for the thickness of an electrode catalyst bed. It is possible to ask for the thickness of an electrode catalyst bed by various technique, without being especially limited besides above–mentioned SEM or above–mentioned SEM–XMA. Since it is the sheet with which the gestalt of an electrode catalyst bed can become independent especially, measuring with the usual thickness meter is possible.

[0020] Since it is the description that catalyst–polymer complex is united with \*\*\*\*\*, the electrode catalyst bed of this invention serves as an embodiment also with desirable it being also the sheet with which the gestalt of an electrode catalyst bed can become independent. The conventional electrode catalyst bed was created by the approach of establishing on the electrode substrate which consists of a porosity electric conduction sheet as mentioned above, or the approach of establishing on the proton exchange film. For this reason, electrode catalyst beds were that completion or before to an electrode substrate or the proton exchange film, and one. It is the description that the electrode catalyst bed of this invention may exist independently from an electrode substrate or the proton exchange film since catalyst–polymer complex is united with \*\*\*\*\*. That is, \*\*\*\*\* has played a role of a core, and when this \*\*\*\*\* carries out on–the–strength maintenance, that gestalt can be maintained as the sheet of an electrode catalyst bed of this invention with which a gestalt can become independent, i.e., other sheet and laminatings and sheets which became independent even if not joined, and it becomes the sheet which that component does not separate and disassemble in self–weight extent. However, in case the electrode catalyst bed of this invention is applied to various electrochemistry equipments, it is joined to an electrode substrate or the proton exchange film, and has become film–electrode complex (MEA), and this distinction of whether in the state of MEA, that gestalt of an electrode catalyst bed is already an independence sheet is difficult.

[0021] As \*\*\*\*\* used for this invention, electric resistance is low and it is possible to use without being limited especially if it is the structure of having the opening of the penetration which a gas tends to penetrate. As a component of the porosity electric conduction sheet of \*\*\*\*\* , that which is mainly concerned with conductive mineral matter is mentioned, for example, and carbon material, such as a baking object from a polyacrylonitrile, a baking object from a pitch, a graphite, and expanded graphite, a stainless steel, molybdenum, titanium, etc. are illustrated as this conductive mineral matter. the case where especially the gestalt of conductive mineral matter is used for the electrochemistry equipment which uses a gas for an electrode active material like a fuel cell although the shape of fibrous or a particle etc. is not limited — the fibrous conductivity mineral matter (inorganic conductivity fiber) from the point of gas permeability — especially a carbon fiber is desirable. as the porosity electric conduction sheet using inorganic conductivity fiber about \*\*\*\*\* — textile fabrics or a nonwoven fabric — any structure is usable. Especially as textile fabrics, plain weave, twill weave, satin, a brocade, figured brocade, etc. are used, without being limited. Moreover, especially as a nonwoven fabric, a paper–making method, the needle punch method, the span bond method, the water jet punching method, the melt blowing method, etc. are used, without being limited. Moreover, you may be knitting. In these textiles, when especially a carbon fiber is used, after [ which twists the textile fabrics which carbonized or graphitized the plain weave fabric using fire resistance–ized spun yarn, and fire resistance–ized yarn by the needle punch method, the water jet

punching method, etc. ] carrying out nonwoven fabric processing, the mat nonwoven fabric by the paper-making method using the nonwoven fabric, the fire resistance-ized yarn, carbonization yarn, or graphitization yarn carbonized or graphitized etc. is used preferably. The point that the textile which has reinforcement thinly especially is obtained to a nonwoven fabric is desirable.

[0022] As eyes of the porosity electric conduction sheet of \*\*\*\*\*, when made from inorganic conductivity fiber, especially a carbon fiber, it is desirable that it is 1 - 30 g/m<sup>2</sup>. In less than two 1 g/m, the reinforcement of a porosity electric conduction sheet becomes low. The porosity electric conduction sheet exceeding 30 g/m<sup>2</sup> becomes thick, and the engine performance as an electrode catalyst bed falls.

[0023] As for the electric resistance of the porosity electric conduction sheet of \*\*\*\*\*, it is desirable that they are two or less 50 ohm-cm as sheet resistivity of the sheet thickness direction. It is two or less 100m ohm-cm further more preferably two or less 1 ohm-cm more preferably. When resistance is high, and especially a porosity electric conduction sheet is thick, the engine performance in an electrode catalyst bed falls.

[0024] Measurement of the electric resistance R of the porosity electric conduction sheet of \*\*\*\*\* is performed by the following approach. Two test electrode plates which copper foil with width of face of 50mm, a die length [ of 200mm ], and a thickness of 0.1mm stuck on one side of the vitrified charcoal blank which has the flat surface where a front face with width of face of 50mm, a die length [ of 200mm ], and a thickness of 1.5mm is smooth are prepared. Uniform spacing is kept substantial and the fields of a vitrified charcoal blank make two test electrode plates counter. The terminal for electrical potential differences is prepared for the terminal for currents in each end of two test electrode plates at each other end. The porosity electric conduction sheet with a diameter of 46mm cut down circularly is inserted in said gap, and it lays in the center section of two test electrode plates. A test electrode plate moves so that the pressure of 0.98MPa(s) may be made to act on the laid sheet. The current of 1A is passed between two test electrode plates from the terminal for currents. With the terminal for electrical potential differences, electrical-potential-difference [ at this time ] V (V) is measured. From the value of the measured electrical potential difference V, Resistance R (momega and cm<sup>2</sup>) is calculated by the degree type.

$R = V \times 2.3 \times 2.3 \times \pi \times 1000$  — here, pi is a circular constant.

[0025] When the inorganic conductivity fiber which consists of a carbon fiber is used as a porosity electric conduction sheet of \*\*\*\*\*, as a carbon fiber, a polyacrylonitrile (PAN) system carbon fiber, a phenol system carbon fiber, a pitch based carbon fiber, a rayon system carbon fiber, etc. are illustrated. Especially, a PAN system carbon fiber is desirable. As for a PAN system carbon fiber, compared with a pitch based carbon fiber, whenever [ compressive-strength and \*\*\*\* breaking extension ] is large, and it cannot break easily. This is considered to be based on the difference of crystallization of the carbon which constitutes a carbon fiber. In order to obtain the carbon fiber into which it is hard to break, the heat treatment temperature of a carbon fiber has desirable 2,500 degrees C or less, and its 2,000 degrees C or less are more desirable.

[0026] As for the diameter of the inorganic conductivity fiber used for the porosity electric conduction sheet of \*\*\*\*\*, it is desirable that it is 20 micrometers or less. 12 micrometers or less are more desirable and 8 micrometers or less are still more desirable. If the diameter of fiber is thick, the thickness of a porosity electric conduction sheet will become thick, and the electrode engine performance will fall.

[0027] The porosity electric conduction sheet of \*\*\*\*\* is an embodiment also with desirable also performing partial hydrofuge \*\* hydrophilic processing for forming the exhaust passage of a water-repellent finish which prevents the gaseous diffusion and the penetrable lowering by stagnation of water and which is performed for accumulating, and water, addition of carbon powder performed in order to lower resistance.

[0028] It is possible to use without being limited especially if it is the structure of having the opening of the penetration which a gas tends to penetrate as a non-conductive textile used for \*\*\*\*\* of this invention. It is used without being limited as a component of a non-conductive textile, for example, especially if it is non-conductive fiber.

[0029] As non-conductive fiber which constitutes the non-conductive textile of \*\*\*\*\* A polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoro ethylene copolymer (FEP), A tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), A tetrafluoroethylene-ethylene copolymer (ETFE), polyvinylidene fluoride (PVDF), The Pori vinyl fluoride (PVF), polychlorotrifluoroethylene resin (CTFE), chlorinated polyethylene, a fire resistance-ized polyacrylonitrile, a polyacrylonitrile, polyester, a polyamide, polyethylene, especially polypropylene, etc. are usable, without being limited. Also in these non-conductive fiber, the fiber which consists of fluorine atom content polymers, such as PTFE, FEP, PFA, ETFE, PVDF, PVF, and CTFE, is desirable from points at the time of electrode reaction, such as corrosion resistance.

[0030] as the non-conductive textile of \*\*\*\*\* — textile fabrics or a nonwoven fabric — any structure is usable. Especially as textile fabrics plain weave, twill weave, satin, a brocade, figured brocade, etc. are used, without being limited. Moreover, especially as a nonwoven fabric, a paper-making method, the needle punch method, the span bond method, the water jet punching method, the melt blowing method, etc. are used, without being limited. Moreover, you may be knitting. In these textiles, the nonwoven fabric by the plain weave fabric, the needle punch method, the water jet punching method, etc., the mat nonwoven fabric by the paper-making method, etc. are used especially preferably. The point that the textile which has reinforcement thinly especially by porosity is obtained to a nonwoven fabric is desirable.

[0031] It is the description that catalyst-polymer complex is united with \*\*\*\*\* (here non-conductive textile), and the description of this invention differs from the structure filled up with the electrode catalyst and the solid polymer electrolyte all over the opening of the conventional non-conductive drawing porosity PTFE. A non-conductive textile has the especially high maintenance engine performance of catalyst-polymer complex compared with the drawing porosity PTFE. For this reason, it ends with fewer spreading or an impregnation process to catalyst spreading to the drawing porosity PTFE and desiccation being multiple-times need. Moreover, to the drawing porosity PTFE being a film-like, by this invention, since it is a textile, it is dealt with, and it has the description that a sex is good and excellent in workability.

[0032] As for the thickness of the non-conductive textile of \*\*\*\*\* , it is desirable that it is 50 micrometers or less like the thickness of an electrode catalyst bed. Moreover, the thickness of non-conductive textile creation time to thin-film-izing is possible by a press etc.

[0033] As eyes of the non-conductive textile of \*\*\*\*\* , when made from inorganic conductivity fiber, especially a carbon fiber, it is desirable that it is 1 – 60 g/m<sup>2</sup>. In less than two 1 g/m, the reinforcement of a porosity electric conduction sheet becomes low. The porosity electric conduction sheet exceeding 60 g/m<sup>2</sup> becomes thick, and the engine performance as an electrode catalyst bed falls.

[0034] As for the diameter of the non-conductive fiber used for the non-conductive textile of \*\*\*\*\* , it is desirable that it is 30 micrometers or less. 20 micrometers or less are more desirable and 10 micrometers or less are still more desirable. If the diameter of fiber is thick, the thickness of a porosity electric conduction sheet will become thick, and the electrode engine performance will fall. However, it is also desirable from the point of thin-film-izing to press a non-conductive textile as mentioned above, and especially the diameter of fiber before a press is not limited.

[0035] The non-conductive textile of \*\*\*\*\* is an embodiment also with desirable also performing partial hydrofuge \*\* hydrophilic processing for forming the exhaust passage of a water-repellent finish which prevents the gaseous diffusion and the penetrable lowering by stagnation of water and which is performed for accumulating, and water, addition of inorganic conductivity powder performed in order to lower resistance.

[0036] The porosity electric conduction sheet of \*\*\*\*\* is an embodiment also with desirable a conductive particle, especially a conductive inorganic particle also being included from points, such as improvement in a consistency, and reduction of electric resistance, when consisting of inorganic conductivity fiber as mentioned above. As such a conductive inorganic particle, the carbon material from electric resistance or a corrosion resistance point, especially a carbon particle are desirable.

[0037] As such a conductive inorganic particle, although carbon black powder, graphite powder, expanded graphite powder, metal powder, ceramic powder, etc. may also be included, the carbon material of carbon black, graphite, or carbonaceous is preferably mentioned from the point of electronic conductivity and corrosion resistance, for example. As such carbon material, carbon black, such as oil furnace black, channel black, lamp black, thermal black, and acetylene black, is desirable from the magnitude of electronic conductivity and specific surface area. as oil furnace black — the Cabot Corp. make — Balkan Peninsula XC-72, the Balkan Peninsula P, black PARUZU 880, black PARUZU 1100, black PARUZU 1300, black PARUZU 2000, and legal one — the KETCHIEN black EC by 400 and LION, and the Mitsubishi Chemical make — #3150, #3250, etc. mention — having — as acetylene black — DIN by DENKI KAGAKU KOGYO K.K. — a turnip — a rack etc. is mentioned. Moreover, there are an artificial graphite, carbon, etc. which are obtained from organic compounds, such as a natural graphite besides carbon black, a pitch, corks, a polyacrylonitrile, phenol resin, and furan resin. Moreover, it is possible to also use the carbon material which carried out after-treatment processing of these carbon material. the inside of such carbon material — especially Balkan Peninsula XC-72 by Cabot Corp., and DIN by DENKI KAGAKU KOGYO K.K. — a turnip — a rack, the LION KETCHIEN black, etc. are preferably used from the point of electronic conductivity.

[0038] In addition, as an addition of the conductive particle to \*\*\*\*\* , it should not be suitably decided according to the specific surface area of the electrode characteristic demanded or the matter used, electronic resistance, etc., and is not especially limited.



[0039] \*\*\*\*\* can also add a polymeric material besides the above-mentioned conductive particle (when mainly coming to have a porosity electric conduction sheet especially). This becomes strong to compression or tension, reinforcement and handling nature are raised, and the inorganic conductivity matter can separate from \*\*\*\*\* or can prevent turning to the thickness direction of \*\*\*\*\*. In case paper making of the inorganic conductivity staple fiber is carried out and \*\*\*\*\* is created especially, it is important to use a polymeric material as a binder. There are an approach of mixing fibrous and a granular and liquefied polymeric material as an approach of making a polymeric material binding, when making the orientation of the inorganic conductivity matter carry out in the random direction into a 2-dimensional flat surface substantially, an approach to which a polymeric material fibrous to the aggregate with which orientation of the inorganic conductivity matter was substantially carried out in the random direction into the 2-dimensional flat surface, and liquefied is made to adhere.

[0040] Especially as a polymeric material which binds the inorganic conductivity matter of \*\*\*\*\* , although not limited, the polymeric material which contains a fluorine atom from the point of the electrode engine performance is used preferably. A polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoropropylene copolymer (FEP), a tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), etc. are used especially preferably.

[0041] As for the content to the porosity electric conduction sheet as \*\*\*\*\* of the above polymeric materials, it is desirable that it is in 0.1 - 50% of the weight of the range. Although little way of the content of a polymeric material is good in order to make low the electric resistance of a porosity electric conduction sheet, at less than 0.1 % of the weight, the reinforcement which is equal to handling runs short, and omission of the inorganic conductivity matter also increase. On the contrary, if it exceeds 40 % of the weight, the problem that the electric resistance of a porosity electric conduction sheet increases will arise. It is 10 - 30% of the weight of the range more preferably.

[0042] The polymeric material added on the porosity electric conduction sheet of \*\*\*\*\* is an embodiment also with desirable also calcinating above 200 degrees C. The above-mentioned fluororesin used for a water-repellent finish is heating more than the melting point, and water repellence and its binding property improve. Moreover, in polymeric materials other than a fluororesin, binding capacity improves by baking, and also lowering of electric resistance and corrosion resistance improvement are found.

[0043] The porosity electric conduction sheet of \*\*\*\*\* may be constituted using a conductive particle and a polymer, without using fiber except that it consists of inorganic conductivity fiber, such as the above-mentioned carbon fiber. As such a conductive particle, carbon particles, such as carbon black and a graphite, are used preferably as mentioned above. Moreover, as a polymer, what contains a fluorine atom as mentioned above is used preferably. Especially the ratio of a conductive particle and a polymer is not limited.

[0044] The non-conductive textile of \*\*\*\*\* can also add a polymeric material besides the above-mentioned conductive particle. This becomes strong to compression or tension, reinforcement and handling nature are raised, and it can prevent that the inorganic conductivity matter separates from a non-conductive textile.

[0045] As for the content to the non-conductive textile of the above polymeric materials, it is desirable that it is in 0.1 - 50% of the weight of the range. Although little way of the content of a polymeric material is good in order to make the electric resistance of a non-conductive textile low, at less than 0.1 % of the weight, the reinforcement which is equal to handling runs short, and omission of the inorganic conductivity matter also increase. It is 10 - 30% of the weight of the range more preferably.

[0046] The non-conductive textile of a support layer is an embodiment also with desirable also performing after treatment, such as heat treatment, a drawing, and a press. Desirable effectiveness, such as thin-film-izing, an increment in voidage, and an increment on the strength, is expectable with such after treatment.

[0047] Especially the electrode catalyst that constitutes the catalyst-polymer complex of this invention can use a well-known thing, without being limited. Although it is not limited especially when using the electrode catalyst bed of this invention for a fuel cell, precious metal catalysts, such as platinum, palladium, gold, a ruthenium, and iridium, are used preferably. Moreover, two or more sorts of elements, such as an alloy of these precious metal catalysts and mixture, may be contained.

[0048] The electrode catalyst of this invention is the object which gives electronic conduction nature and is distributed efficiently, and is an embodiment also with desirable also being used after having been supported by the conductive particle. As a conductive particle which supports an electrode catalyst, carbon material, such as carbon black, is desirable. As such carbon material, carbon black, such as oil furnace black, channel black, lamp black, thermal black, and acetylene black, is desirable from the magnitude of electronic conductivity and specific surface area. as oil furnace black — the Cabot Corp.

make — Balkan Peninsula XC-72, the Balkan Peninsula P, black PARUZU 100, black PARUZU 1100, black PARUZU 1300, black PARUZU 1500, and legal one — the KETCHIEN black C by 400 and LION, and the Mitsubishi Chemical make — #3150, #3250, etc. mention — having — as acetylene black — DIN by DENKI KAGAKU KOGYO K.K. — a turnip — a rack etc. is mentioned. Moreover, there are an artificial graphite, carbon, etc. which are obtained from organic compounds, such as a natural graphite besides carbon black, a pitch, corks, a polyacrylonitrile, phenol resin, and furan resin. As a gestalt of these carbon material, it can use fibrous besides the shape of a particle. Moreover, it is possible to also use the carbon material which carried out after-treatment processing of these carbon material. Also in such carbon material, Balkan Peninsula XC-72 by Cabot Corp. are especially used preferably from the point of electronic conductivity. The amount of support of the electrode catalyst over a conductive particle has 5 – 80 desirable % of the weight, and is desirable. [ especially 20 – 60% of ] case there are few amounts of support — an electrode catalyst bed — \*\* — since the electrode engine performance falls when it becomes thick highly, and the dispersibility of catalyst-polymer complex becomes poor, in many, it is not desirable.

[0049] Although it is suitably chosen as a polymer contained in the catalyst-polymer complex of this invention according to the electrode engine performance called for and is not limited especially, the polymer containing a fluorine atom is desirable. a copolymer with the monomer of others as such a fluorine atom content polymer, such as these copolymers, such as the Pori polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoropropylene copolymer (FEP), tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), polyvinylidene fluoride (PVDF), vinyl, etc. fluoride (PVF), or these monomeric units, ethylene, and styrene, — a blend etc. can be used further.

[0050] Moreover, the polymer which has a proton exchange group as a polymer contained in the catalyst-polymer complex of this invention is used still more preferably. As a proton exchange group, a sulfonic group, a carboxylic-acid radical, a phosphoric-acid radical, etc. are used suitably and preferably. The polymer which has the proton exchange group which consists of a fluoro alkyl ether side chain and a fluoro alkyl principal chain especially is used most preferably. For example, Nafion made from DuPont, Aciplex by Asahi Chemical Co., Ltd., Flemion by Asahi Glass Co., Ltd., etc. are desirable. Catalyst-polymer complex is constituted by mixing these proton exchange group content polymers with an electrode catalyst in the state of a solution or dispersion liquid. In this case, although especially the solvent that dissolves or decentralizes a proton exchange group content polymer is not limited, the soluble point of a proton exchange group content polymer to a polar solvent is desirable. You may be other polymers, such as a polymer, ethylene, styrene, etc. containing the above-mentioned fluorine atom which has a proton exchange group, these copolymers, and a blend.

[0051] Although the ratio of the electrode catalyst in catalyst-polymer complex and a polymer should not be suitably decided according to whenever [ ionic conduction / of the electrode characteristic demanded or the proton exchange group content polymer used ] etc. and is not limited especially, it is desirable at a weight ratio, and is still more desirable. [ 5 – 50% of ] [ 1 – 80% of ] It is that the structure where catalyst-polymer complex and \*\*\*\*\* are united becomes weak when there are few polymers, and the point which ionic conductivity becomes low, and checks gas permeability when many, and the electrode engine performance is all reduced.

[0052] To the catalyst-polymer complex of this invention, it is also desirable to add the various matter else [ , such as an above-mentioned electrode catalyst, electrode catalyst support carbon, or a polymer, ]. Especially, it also becomes a desirable embodiment from the point on an electronic conduction disposition to add an electric conduction agent. Especially as such an electric conduction agent, although not limited, carbon particles, such as above-mentioned carbon black, are used preferably. Although it should be suitably decided as an addition of these electric conduction agent according to the specific surface area of the electrode characteristic demanded or the matter used, electronic resistance, etc., 1 – 80% is desirable as a weight ratio in an electrode catalyst bed, and 10 – 30% is still more desirable. Electronic resistance becomes low, when there are few electronic conductors, when many, gas permeability is checked, and also all reduce the electrode engine performance — a catalyst utilization factor falls.

[0053] It is an embodiment also with desirable the catalyst-polymer complex contained in the electrode catalyst bed of this invention also having three-dimensions mesh fine porous structure. In addition, "three-dimensions mesh fine porosity structure" means the condition of having the network structure of the shape of three dimensions with which catalyst-polymer complex was connected in three dimensions.

[0054] When the catalyst-polymer complex contained in an electrode catalyst bed has three-dimensions mesh fine porous structure, it is desirable that the diameter of fine porosity is 0.05–5 micrometers. It is 0.1–1 micrometer more preferably. The diameter of fine porosity is a scanning electron microscope (SEM) etc., and from the photograph which photoed the front face, it can ask for it from the average of 100 or

more pieces preferably 20 or more pieces, and it can usually be measured by 100 pieces. Since distribution of the diameter of fine porosity is large, as for the catalyst bed of the fine porous structure of this invention at the time of being manufactured by the wet solidifying method, it is desirable to take the average of as many apertures as possible.

[0055] As for the void content of three-dimensions mesh fine porous structure, it is desirable that it is 10 – 95%. It is 50 – 90% more preferably. A void content is the percentage (%) and  $= (V1 - V2) / V1 \times 100$  which is calculated by V1 what subtracted the volume (V2) which catalyst-polymer complex occupies further from the remaining volume (V1) which subtracted the volume which a porosity electric conduction sheet occupies from the whole catalyst bed product.

[0056] A void content is large and electronic conduction nature and its proton conductivity are [ the thing of the three-dimensions mesh fine porous structure by which especially the catalyst-polymer complex contained in an electrode catalyst bed was created by the wet solidifying method has good blowdown of gaseous diffusion nature or generation water, and ] also good. Although making a hole form using an ostomy agent etc. is performed in the conventional porosity-ization or it increases catalyst particle diameter and the particle diameter of an addition polymer, the contact resistance between catalyst support carbon and between proton exchange resin will become large compared with an electrode catalyst bed by such porosity-ized method. Since the polymer complex which contained catalyst support carbon to it with the three-dimensions mesh fine porous structure by the wet solidifying method has become three-dimensions mesh-like, an electron and a proton tend to conduct this polymer complex, and blowdown of gaseous diffusion nature or generation water also has good structure further for fine porous structure.

[0057] When the catalyst-polymer complex contained in an electrode catalyst bed has three-dimensions fine porous structure, the matter used for a catalyst, an electronic conductor, and a proton conductor can use the same matter as usual. However, in case the electrode catalyst bed which has three-dimensions mesh fine porous structure is created, being based on the wet solidifying method is desirable. Therefore, in the aforementioned case, it is desirable to use the polymer suitable for this wet solidifying method, and it is desirable to use the polymer which distributes a catalyst particle well and does not deteriorate in the oxidation-reducing atmosphere in a fuel cell. Although the polymer containing a fluorine atom is mentioned as such a polymer and it is not limited especially, for example The polymer which has the proton exchange group which consists of a fluoro alkyl ether side chain and a fluoro alkyl principal chain is used most preferably. To others, the Pori vinyl fluoride (PVF), polyvinylidene fluoride (PVDF), Poly hexafluoropropylene (FEP), polyperfluoro alkyl vinyl ether (PFA), etc., or the copolymer (for example, hexafluoropropylene-vinylidene fluoride copolymer) of these copolymers, these monomeric units, and other monomers, such as ethylene and styrene, — a blend etc. can be used further.

[0058] The polymer which has also in this the proton exchange group which consists of a fluoro alkyl ether side chain and a fluoro alkyl principal chain is the most desirable, and it is Du. The thing melted to alcohol, water, or other polar solvents by using Nafion made from Pont, Aciplex by Asahi Chemical Co., Ltd., Flemion by Asahi Glass Co., Ltd., etc. as a good solvent (dissolution solvent) or the dispersed thing is used preferably. An electrode catalyst may be added to these solutions, it kneads, wet coagulation is performed by making a poor solvent (coagulation solvent) contact, and the catalyst-polymer complex which has three-dimensions fine porous structure is created. Although polar solvents, such as water, methanol, ethanol, i-propanol, N-methyl-2-pyrrolidone, N, and N-dimethyl sulfoxide and dimethyl imidazolidinone, are mentioned and low dielectric constant solvents, such as cyclic ether, such as ester, such as butyl acetate, ethyl acetate, isobutyl acetate, methyl propionate, ethyl propionate, dimethyl carbonate, diethyl carbonate, and methylethyl carbonate, a tetrahydrofuran, and dioxane, are mentioned as a poor solvent as a good solvent, it is not limited to these.

[0059] Moreover, as a polymer of catalyst-polymer complex, in using polyvinylidene fluoride (PVDF), a hexafluoropropylene-vinylidene fluoride copolymer, etc., aprotic polar solvents, such as N-methyl-2-pyrrolidone, N, and N-dimethyl sulfoxide, dimethyl imidazolidinone, and dimethyl sulfoxide, are mentioned as a good solvent, and it performs the wet solidifying method which uses protonic polar solvents, such as water, a methanol, ethanol, and i-propanol, as a coagulation solvent. When these polymers are used, it is desirable to add an above-mentioned proton conductor for the improvement in proton conductivity in an electrode catalyst bed.

[0060] As for the polymer used for catalyst-polymer complex, copolymerization or blending and using are also desirable in the polymer containing the above-mentioned fluorine atom, or the polymer containing a proton exchange group. Especially the thing for which polymers, such as Nafion which has a fluoro alkyl ether side chain and a fluoro alkyl principal chain in a proton exchange group, are blended with polyvinylidene fluoride, the Pori (hexafluoropropylene-vinylidene fluoride) copolymer, etc. is desirable from

the point of the electrode engine performance.

[0061] Although the main components of catalyst-polymer complex are catalyst support carbon and a polymer suitably, and those ratios should especially be suitably decided according to the electrode characteristic needed and it is not limited, 5 / 95 - 95/5 are preferably used by the weight ratio of catalyst support carbon / polymer. When using as an electrode catalyst bed for polymer electrolyte fuel cells especially, 40 / 60 - 85/15 are desirable by catalyst support carbon / polymer weight ratio.

[0062] Especially as an approach of making catalyst-polymer complex uniting with \*\*\*\*\*, although not limited, an impregnation method, the applying method, etc. are desirable approaches. An impregnation method is immersed in \*\*\*\*\* into the liquid with which catalyst-polymer complex or its precursor is contained, and is performed by making catalyst-polymer complex permeate all over the opening of \*\*\*\*\*. In addition, it is not limited, especially although the precursor of catalyst-polymer complex is the ingredient which can form the complex concerned by the time formation of an electrode catalyst bed or a fuel cell electrode is completed, for example, the mixture of a catalyst, the mixed solution of a polymer and a catalyst, and the monomer of a polymer etc. can be illustrated. The applying method is performed by carrying out coating of the liquid with which catalyst-polymer complex is contained on \*\*\*\*\* etc. Although it should not be limited especially about the coating approach, the general methods of application, such as a knife coating machine, a bar coating machine, a spray, a dip coater, a spin coater, a roll coater, a die coating machine, a curtain coating machine, and brush coating, are used. The solvent of the liquid with which catalyst-polymer complex is contained in the case of which [ of an impregnation method and the applying method ], viscosity, solid content, etc. are suitably chosen by neither the voidage of \*\*\*\*\*, nor the surface state of the matter to constitute, and may not be limited especially.

[0063] The electrode catalyst bed of this invention is the embodiment of this invention also with desirable also constituting film-electrode complex (MEA:Membrane Electrode Assembly) with the proton exchange film and an electrode substrate.

[0064] Although especially the proton exchange film used for the film-electrode complex of this invention is not limited, its polymer of fluorine atom content is desirable from a viewpoint of the endurance in the oxidation-reducing atmosphere in an electrode. Moreover, it is not limited [ radical / a sulfonic group a carboxylic-acid radical, / phosphoric-acid ] especially as a proton exchange group of the proton exchange film.

[0065] Although this proton exchange film should be suitably chosen according to the application and the environment where it is divided roughly into the perfluoro system of the copolymer which consists of a hydrocarbon system, and a fluorine atom content polymer especially a fluoro alkyl ether side chain and fluoro alkyl principal chains, such as a styrene-divinylbenzene copolymer which has the above-mentioned proton exchange group, especially a sulfonic group, and a fuel cell is used, a fluorine atom content polymer, especially its perfluoro system are desirable from the point of a fuel cell life. Moreover, the partial fluorine film which carried out the fluorine atom permutation selectively is also used preferably. By the perfluoro film, Nafion made from DuPont, Asahi Chemical Aciplex, Asahi Glass Flemion, Japan Gore-Tex Goa-select, etc. are illustrated, and there are some which introduced the sulfonic group into the polymer and polyvinylidene fluoride of a trifluoro styrene sulfonic acid in the partial fluorine film. Moreover, the proton exchange film can use one sort of not only polymers but the bipolar membrane which stuck the copolymer of two or more sorts of polymers, and blend polymer and two or more sorts of film, the film which reinforced the proton exchange film with the nonwoven fabric, the porous film, etc.

[0066] Although electric resistance is low and it is possible to use without being limited especially if \*\* (\*\*) \*\* can be performed as an electrode substrate used for the film-electrode complex of this invention, the description of this invention is discovered especially in a porosity electric conduction sheet. The conductive porosity sheet used for an electrode substrate can be applied without differing from the porosity electric conduction sheet used for the above-mentioned electrode catalyst bed in any way. However, to the thickness of the porosity electric conduction sheet used for an electrode catalyst bed being 50 micrometers or less, the thickness of the porosity electric conduction sheet used for an electrode substrate is desirable 50-400 micrometers, and it is used. The conductive porosity sheet used for an electrode substrate has good gas permeability, and can be used, without being limited especially if it is a sheet with low electric resistance.

[0067] As a component of an electrode substrate, that which is mainly concerned with conductive mineral matter is mentioned, for example, and carbon material, such as a baking object from a polyacrylonitrile, a baking object from a pitch, a graphite, and expanded graphite, a stainless steel, molybdenum, titanium, etc. are illustrated as this conductive mineral matter. the case where especially the gestalt of conductive mineral matter is used for the electrochemistry equipment which uses a gas for an electrode active

material like a fuel cell although the shape of fibrous or a particle etc. is limited — the fibrous conductivity mineral matter (inorganic conductivity fiber) from the point of permeability — especially a carbon fiber is desirable. as the porosity electric conduction sheet using inorganic conductivity fiber — textile fabrics or a nonwoven fabric — any structure is usable. For example, the carbon cross made from the carbon paper TGP series by Toray Industries, Inc., SO series, and E-TEK etc. is used.

[0068] That whose thickness when applying the uniform planar pressure of 2.9MPa(s) in the thickness direction is 0.05–0.4mm as an electrode substrate used for this invention is desirable. It is 0.08–0.2mm more preferably. When thinner than 0.05mm, in case it uses for a fuel cell, an electrode substrate is buried in the gas passageway of a separator, the diffusion and permeability to the direction of a field become low, and reinforcement becomes it is weak and lacking in workability. When thicker than 0.4mm, the electric resistance of the thickness direction increases. In addition, thickness sandwiches an electrode substrate by the vitrified charcoal blank of two sheets which has a smooth front face by uniform thickness, and pressurizes it by the uniform planar pressure of 2.9MPa, and it asks for it from the difference of spacing of a vitrified charcoal blank with the time of inserting with the time of not inserting an electrode substrate.

[0069] It is desirable that it is 10 – 220 g/m<sup>2</sup> as eyes of an electrode substrate. It is 20 – 120 g/m<sup>2</sup> more preferably. In less than two 10 g/m, the reinforcement of an electrode substrate becomes low. Moreover, when it constructs on the polyelectrolyte film, a catalyst bed, and the time of unification of an electrode substrate and a cell, an electrode substrate becomes thin and the diffusion / transparency effectiveness to the direction of a field becomes imperfection. When 220 g/m<sup>2</sup> was exceeded and it constructs on a cell, an electrode substrate becomes thick and resistance becomes large.

[0070] When the uniform planar pressure of 2.9MPa(s) is applied in the thickness direction, as for the consistency of an electrode substrate, it is desirable that it is 0.3 – 0.8 g/cm<sup>3</sup>. 0.35 – 0.7 g/cm<sup>3</sup> is more desirable, and 0.4 – 0.6 g/cm<sup>3</sup> is still more desirable. It asks for the consistency of the electrode substrate when applying the uniform planar pressure of 2.9MPa(s) in the thickness direction by count from the thickness of the electrode substrate when applying the uniform planar pressure of 2.9MPa(s) in the eyes and the thickness direction of an electrode substrate. In order for an electrode substrate to make diffusion and permeability high, it is necessary to make porosity high but, and if the consistency when applying the uniform planar pressure of 2.9MPa(s) in the thickness direction becomes larger than 0.8 g/cm<sup>3</sup>, porosity will fall and diffusion and permeability will become imperfection. Moreover, if smaller than 0.3 g/cm<sup>3</sup>, the resistance of the thickness direction will become large.

[0071] As for an electrode substrate, it is desirable that the pressure loss at the time of making 14cm [ /second ] air penetrate in the thickness direction in the condition of not performing application of pressure by the planar pressure to the thickness direction is below 98Pa (10mmAq) in respect of the gaseous diffusion nature of an electrode substrate. Below 29Pa (3mmAq) is more desirable, and below 9.8Pa (1mmAq) is still more desirable.

[0072] More than the 0.49N/10mm width of face of the tensile strength of an electrode substrate is desirable, more than its 1.96N/10mm width of face is more desirable, and more than its 4.9N/10mm width of face is still more desirable. When tensile strength is low, there is a problem that possibility that a sheet will be damaged increases, in high order processing of electrode equipment and materials.

[0073] It is desirable that it is two or less 100m ohm-cm, as for the electric resistance of a porosity conductive liner sheet, it is more desirable that it is two or less 50m ohm-cm, and it is still more desirable that it is two or less 15m ohm-cm. It is desirable that it is two or less 150m ohm-cm, as for the electric resistance of the electrode substrate which contains a water-repellent fluororesin like the after-mentioned, it is more desirable that it is below 70m ohm-cm, and it is still more desirable that it is two or less 30m ohm-cm.

[0074] In addition to the above, the porosity electric conduction sheet the die length of inorganic conductivity fiber is at least 3mm, and is [ sheet ] at least 5 times the thickness of a sheet can also be used for an electrode substrate including the paper-like sheet which comes to bind with a polymeric material the inorganic conductivity fiber by which orientation was substantially carried out in the random direction into the 2-dimensional flat surface. Here, the thickness of a sheet is measured according to JISP8118. Planar pressure at the time of measurement is taken as 13kPa(s). The semantics of saying [ that orientation of the inorganic conductivity fiber is substantially carried out into a 2-dimensional flat surface ] means that it lies so that inorganic conductivity fiber may form one field in general. The short circuit with a counter electrode and the breakage of inorganic conductivity fiber by inorganic conductivity fiber can be prevented by this.

[0075] In order to make the reinforcement and handling nature of an electrode substrate high and to carry out orientation of the inorganic conductivity fiber into a 2-dimensional flat surface substantially, the die

length of inorganic conductivity fiber has at least 3 desirable mm or more and it sets it to 6 mm or more still more preferably 4.5 mm or more more preferably. In less than 3 mm, it becomes difficult to maintain reinforcement and handling nature. However, it may also be desirable to mix the inorganic conductivity fiber from which fiber length differs, it may be desirable that the inorganic conductivity fiber of long fiber length is 3 mm or more in this case, and the inorganic conductivity fiber of short fiber length may be less than 3 mm. Moreover, in order to make the orientation of the inorganic conductivity fiber carry out in the random direction into a 2-dimensional flat surface substantially, the die length of inorganic conductivity fiber is preferably made into 12 or more times still more preferably 8 or more times 5 or more-time thick Mino of an electrode substrate. In less than 5 times, reservation of two-dimension orientation becomes difficult. In order to make the orientation of the upper limit of the die length of inorganic conductivity fiber carry out in the random direction into a 2-dimensional flat surface substantially, its 30 mm or less is desirable, and it is more desirable, and is still more desirable. [ of 8 mm or less ] [ of 15 mm or less ] If inorganic conductivity fiber is too long, it will be easy to generate a maldistribution, and while much fiber has been bundles-like, it may remain. In that case, a bundle-like part has low voidage, since the thickness at the time of application of pressure becomes thick, a high pressure is applied at the time of application of pressure, and problems, such as destruction of an electrode substrate, polyelectrolyte film, and local lamination of an electrode catalyst bed, become easy to arise.

[0076] In creation of an electrode substrate, there are a wet method which is made to distribute inorganic conductivity fiber and mills paper in the medium of a liquid, and dry process which is made to distribute inorganic conductivity fiber and is made to lie in air as an approach of making the orientation of the inorganic conductivity fiber carrying out in the random direction into a 2-dimensional flat surface substantially. In order to carry out orientation of the inorganic conductivity fiber into a 2-dimensional flat surface substantially certainly, and in order to make reinforcement of inorganic conductivity fiber high, a wet method, especially the so-called paper-making method are desirable.

[0077] When the inorganic conductivity fiber used for an electrode substrate is a carbon fiber, a polyacrylonitrile (PAN) system carbon fiber, a phenol system carbon fiber, a pitch based carbon fiber, a rayon system carbon fiber, etc. are illustrated. Especially, a PAN system carbon fiber is desirable. As for a PAN system carbon fiber, compared with a pitch based carbon fiber, whenever [ compressive-strength and \*\*\*\* breaking extension ] is large, and it cannot break easily. This is considered to be based on the difference of crystallization of the carbon which constitutes a carbon fiber. In order to obtain the carbon fiber into which it is hard to break, the heat treatment temperature of a carbon fiber has desirable 2,500 degrees C or less, and its 2,000 degrees C or less are more desirable.

[0078] The carbon staple fiber used into the electrode substrate of this invention is good for a diameter D (micrometer), tensile strength  $\sigma$  (MPa), and relation with a modulus of elasticity in tension E (MPa) to have satisfied the degree type. The electrode substrate which consists of such a carbon staple fiber is for being hard to break. Namely, the diameter of a carbon staple fiber is thin, tensile strength is strong, as for a carbon staple fiber, the one where a modulus of elasticity in tension is lower cannot break easily, and an electrode substrate stops being able to break easily at the time of application of pressure.

$\sigma/(ExD) \geq 0.5 \times 10^{-3}$  — here — the tensile strength of a carbon fiber, and a modulus of elasticity in tension — JIS It measures according to R7601. In the case of the flat carbon fiber of a cross section, let the average  $(a+b)/2$  of a major axis (a) and a minor axis (b) be a diameter. When the carbon staple fiber with which classes differ is mixed, the value which carried out the weighted mean about D,  $\sigma$ , and E, respectively is used. It is  $\sigma/(ExD) \geq 1.1 \times 10^{-3}$  preferably, and is  $\sigma/(ExD) \geq 2.4 \times 10^{-3}$  more preferably.

[0079] Whenever [ \*\*\*\* breaking extension / of a carbon staple fiber ] is 1.2% or more preferably [ that it is 0.7% or more ] because of the reinforcement of an electrode substrate, and more preferably, and is 1.8% or more still more preferably. Whenever [ \*\*\*\* breaking extension ] is the value which \*(ed) tensile strength ( $\sigma$ ) by the modulus of elasticity in tension (E).

[0080] As for the diameter of the inorganic conductivity fiber used for an electrode substrate, it is desirable that it is 20 micrometers or less. 12 micrometers or less are more desirable and 8 micrometers or less are still more desirable. On the surface of an electrode substrate, an opening 5 to 10 times the diameter of the diameter of inorganic conductivity fiber is observed. This opening will become large if the diameter of fiber becomes thick.

[0081] Below 200 micro ohm-m of the volume resistivity of the inorganic conductivity fiber used for an electrode substrate is desirable because of the reduction in resistance of an electrode substrate, below its 50 micro ohm-m is more desirable, and below its 15 micro ohm-m is still more desirable. Measurement of the volume resistivity of inorganic conductivity fiber is JIS. It carries out according to R7601. When the fiber



length defined by said measurement formula is not obtained, it measures with the obtained fiber length.

[0082] An electrode substrate in embodiment also with desirable also forming partial hydrofuge \*\* hydrophilic processing for forming the exhaust passage of a water-repellent finish which prevents the gaseous diffusion and the penetrable lowering by stagnation of water and which is performed for accumulating, and water, addition of carbonaceous powder performed in order to lower resistance.

[0083] An electrode substrate is an embodiment also with desirable a conductive particle, especially a conductive inorganic particle also being included from points, such as thickness lowering control at the time of compression, improvement in a consistency, and reduction of electric resistance, when using the porosity electric conduction sheet which consists of a conductive inorganic fiber as mentioned above. As such a conductive inorganic particle, the carbon material from electric resistance or a corrosion resistance point, especially a carbon particle are desirable.

[0084] It is also desirable to use for an electrode substrate the porosity electric conduction sheet with which it comes to arrange the conductive inorganic particle which has flexibility especially in the shape of a sheet. Thereby, there are few omission of a constituent, or even if mechanical force acts, it is hard to break, and the object of electric resistance of offering a cheap electrode substrate low becomes possible. The above-mentioned object can be attained by using an expanded graphite particle as a conductive inorganic particle which has flexibility especially.

[0085] Here, an expanded graphite particle means the graphite particle which a graphite particle is made to expand by heating quickly after being intercalation-compound-ized with a sulfuric acid, a nitric acid, etc., and is obtained. Usually, the distance between layers in the crystal structure of an expanded graphite particle is that [ about 50 to 500 times ] of a raw material graphite particle.

[0086] An expanded graphite particle is rich in the deformans of a configuration in itself. This property is expressed by the language called flexibility. This flexibility is observed by the gestalt-compatibility of the expanded graphite particle to other bodies which adjoin an expanded graphite particle and it. If expanded graphite particles receive an application-of-pressure operation after at least parts have overlapped, according to an application-of-pressure condition, this gestalt-compatibility will deform mutually, and when particles join selectively at least, it will be observed. Moreover, the nominal member used when they are made to arrange this gestalt-compatibility in the shape of a sheet in an expanded graphite particle and the condition that permeability is secured for example, the conductive inorganic particle which does not have the flexibility used conventionally [ such as carbon black, ] — Or when the inorganic conductivity fiber used conventionally [ such as a carbon fiber, ] is both pressurized, in accordance with the shape of an appearance of a nominal member, an expanded graphite particle is transformed and is observed by being joined to this nominal member.

[0087] Although the electrode substrate of this invention is an embodiment also with desirable other conductive particles and conductive fiber also being included in addition to the conductive particle which has flexibility, the electrode substrate the both sides of this conductive fiber and a conductive particle excelled [ electrode substrate ] in thermal resistance, oxidation resistance, and elution-proof nature by consisting of an inorganic material is obtained. As a conductive inorganic particle which does not have flexibility, although carbon black powder, graphite powder, metal powder, ceramic powder, etc. may also be included, the carbon material of carbon black, graphite, or carbonaceous is preferably mentioned from the point of electronic conductivity and corrosion resistance, for example. As such carbon material, carbon black, such as oil furnace black, channel black, lamp black, thermal black, and acetylene black, is desirable from the magnitude of electronic conductivity and specific surface area. as oil furnace black — the Cabot Corp. make — Balkan Peninsula XC-72, the Balkan Peninsula P, black PARUZU 880, black PARUZU 1100, black PARUZU 1300, black PARUZU 2000, and legal one — the KETCHIEN black EC by 400 and LION, and the Mitsubishi Chemical make — #3150, #3250, etc. mention — having — as acetylene black — DIN by DENKI KAGAKU KOGYO K.K. — a turnip — a rack etc. is mentioned. Moreover, there are an artificial graphite, carbon, etc. which are obtained from organic compounds, such as a natural graphite besides carbon black, a pitch, corks, a polyacrylonitrile, phenol resin, and furan resin. Moreover, it is possible to also use the carbon material which carried out after-treatment processing of these carbon material. the inside of such carbon material — especially Balkan Peninsula XC-72 by Cabot Corp., and DIN by DENKI KAGAKU KOGYO K.K. — a turnip — a rack, the LION KETCHIEN black, etc. are preferably used from the point of electronic conductivity.

[0088] In addition, although it should be suitably decided as an addition of the conductive particle to an electrode substrate according to the specific surface area of the electrode characteristic demanded or the matter used, electronic resistance, etc., 1 – 80% is desirable as a weight ratio in an electrode substrate, and 20 – 60% is still more desirable. When there are few electronic conductors, electronic resistance

becomes low, and when many, reduce the electrode engine performance such as checking gas permeability.

[0089] An electrode substrate can also add a polymeric material besides the above-mentioned conductive particle. This becomes strong to compression or tension, reinforcement and handling nature are raised, and the inorganic conductivity matter can separate from an electrode substrate, or can prevent turning to the thickness direction of an electrode substrate. In case the electrode substrate which carries out paper making of the inorganic conductivity staple fiber, and consists of a porosity electric conduction sheet especially is created, it is important to use a polymeric material as a binder. There are an approach of mixing fibrous and a granular and liquefied polymeric material as an approach of making a polymeric material binding, when making the orientation of the inorganic conductivity matter carry out in the random direction into a 2-dimensional flat surface substantially, an approach to which a polymeric material fibrous to the aggregate with which orientation of the inorganic conductivity matter was substantially carried out in the random direction into the 2-dimensional flat surface, and liquefied is made to adhere. What the particle of a polymeric material can distribute and can be substantially dealt with as a liquid in a solvent with the solution which the polymeric material is dissolving is contained in a liquefied concept.

[0090] As a polymeric material which binds the inorganic conductivity matter The polymeric material which has carbon or silicon in a principal chain is desirable. For example, polyvinyl alcohol (PVA), Polyvinyl acetate (vinyl acetate), polyethylene terephthalate (PET), Polypropylene (PP), polyethylene, polystyrene, a polyvinyl chloride, Thermoplastics, such as a polyvinylidene chloride, acrylic resin, and polyurethane, Phenol resin, an epoxy resin, melamine resin, a urea-resin, alkyd resin, Others [ thermosetting resin /, such as an unsaturated polyester resin, acrylic resin, and polyurethane resin, ], Elastomers, such as thermoplastic elastomer, Butadiene Styrene (SBR), and Butadiene Acrylonitrile (NBR), rubber, a cellulose, pulp, etc. can be used. Water-repellent treatment of an electrode substrate may be performed to binding of the inorganic conductivity matter and coincidence using water-repellent resin, such as a fluororesin.

[0091] When the film-electrode complex of this invention is used as a polymer electrolyte fuel cell, in a cathode (an air pole, oxygen pole), the water as an electrode reaction product and the water which permeated the electrolyte are generated. Moreover, in an anode (fuel electrode), a fuel is humidified and supplied for desiccation prevention of the polyelectrolyte film. Since it becomes the hindrance at the time of dew condensation of these water and swelling of the polymeric material by stagnation and water supplying an electrode reaction object, the lower one of the water absorption of the polymeric material contained in an electrode substrate is good. It is 7% or less more preferably 20% or less.

[0092] It is also a desirable embodiment that a water-repellent macromolecule is included in an electrode substrate from such a point. Since the polymer (fluororesin) which contains fluorine atoms, such as a polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoropropylene copolymer (FEP) and a tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), especially has high water repellence, it is used preferably.

[0093] As for the content to the electrode substrate of the above polymeric materials, it is desirable that it is in 0.1 – 50% of the weight of the range. Although little way of the content of a polymeric material is good in order to make the electric resistance of an electrode substrate low, at less than 0.1 % of the weight, the reinforcement which is equal to handling runs short, and omission of the inorganic conductivity matter also increase. On the contrary, if it exceeds 50 % of the weight, the problem that the electric resistance of an electrode substrate increases will arise. It is 10 – 30% of the weight of the range more preferably.

[0094] The polymeric material added to the electrode substrate is an embodiment also with desirable also calcinating above 200 degrees C. The above-mentioned fluororesin used for a water-repellent finish is heating more than the melting point, and water repellence and its binding property improve. Moreover, in polymeric materials other than a fluororesin, binding capacity improves by baking, and also lowering of electric resistance and corrosion resistance improvement are found. Especially in polymeric materials other than a fluororesin, it may be lacking in oxidation resistance, and in case it uses as electrodes for electrochemistry equipments, such as a fuel cell, electrode performance degradation may be brought about while in use. For this reason, it is desirable to calcinate, before using it for electrode creation time as an electrode, using the polymeric-material matter as a binder, and to process carbonization or decomposition clearance.

[0095] It is not limited especially as the manufacture approach of the film-electrode complex of this invention. Generally, although a laminating is carried out and it joins in the order of an electrode substrate, an electrode catalyst bed, the proton exchange film, an electrode catalyst bed, and an electrode substrate, according to the property of an electrode catalyst bed or electrochemistry equipment, it should be suitably decided also about this junction condition. as the junction approach — warming — a press is a desirable



approach, although not limited especially about this condition, either, pressure temperature is 20 degrees C - 200 degrees C, and a pressure is 1 MPa-20 MPa.

[0096] The film-electrode complex (MEA) which consists of the electrode which consists of the electrode catalyst bed and electrode substrate of this invention or this electrode, and proton exchange film can be adapted for various electrochemistry equipments. Inside or a fuel cell, and a water electrolysis layer are desirable, and still more suitable for a polymer electrolyte fuel cell also in a fuel cell. Although there are what uses hydrogen as a fuel, and a thing which uses hydrocarbons, such as a methanol, as a fuel in a fuel cell, it can use without being limited especially.

[0097] Furthermore, although it thinks especially as an application of the fuel cell using the electrode catalyst bed of this invention, without being limited, in a polymer electrolyte fuel cell, the power supply source of the mobile which is a useful application is desirable. It is a mobile with automobiles, such as a passenger car, a bus, and a truck, especially desirable a marine vessel, a railroad, etc.

[0098]

[Example] It explains further using an example per detail of this invention below.

[0099] The creation PAN system carbon fiber (Toray Industries make trading card T-300) of an example 1 (1) porosity electric conduction sheet was judged to 3mm. Water was made to distribute this staple fiber carbon fiber with vinylon. The carbon fiber paper-making object was created by carrying out paper making of these dispersion liquid on a wire gauze.

[0100] Next, it sank into PFA dispersion (neo chlorofluorocarbon PFA dispersion by Daikin Industries, LTD.), and this paper-making object was dried. Furthermore, heat treatment was performed at 370 degrees C for 3 hours, and the porosity electric conduction sheet which consists of a PAN system carbon staple fiber to which PFA adhered 3% of the weight was created. The eyes of this porosity electric conduction sheet were 3 g/m<sup>2</sup>, and thickness was 20 micrometers.

[0101] (2) Catalyst support carbon (catalyst ;P. t, VulcanXC made from carbon; Cabot- 72, amount of platinum support; 30wt%) 2g and i-propanol were added to 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, and the dispersion liquid which stir well and contain catalyst-polymer complex were prepared.

[0102] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the porosity electric conduction sheet created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which a porosity electric conduction sheet and catalyst-polymer complex became integral construction was created. The thickness of 30 micrometers and platinum were attached, amount; 0.5 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount; 0.2 mg/cm<sup>2</sup>.

[0103] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber spun-yarn textiles (20% of amounts [ ELAT made from E-TEK and PFA attached. ]) which gave a water-repellent finish as electrode substrates, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 120 degrees C, pressure 50 MPa).

[0104] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 60 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 600 mW/cm<sup>2</sup>.

[0105] In the coating example 1 (2) of the example 1 (1) catalyst bed of a comparison, the electrode substrate with a catalyst bed (the thickness of 40 micrometers and platinum attached 0.5mg /of 2 and Nafion(s) attached [ Amount; ] cm amount; 0.2 mg/cm<sup>2</sup>) was created screen coating and by drying on the electrode substrate which used the dispersion liquid containing the catalyst-polymer complex created without adding i-propanol in the example 1.

[0106] (2) Two electrode substrates with a catalyst bed created with creation and the assessment above (1) of film-electrode complex and the proton exchange film used in the example 1 were prepared. The catalyst bed was made to counter the proton exchange film, the laminating of an electrode substrate with a catalyst bed / proton exchange film / the electrode substrate with a catalyst bed was carried out in this order, and film-electrode complex was created by performing a heat press like an example 1.

[0107] An example 1 and these conditions created and estimated the polymer electrolyte fuel cell cel for this film-electrode complex. The horsepower outputs were 200 mW/cm<sup>2</sup> and were the bad engine performance compared with the example 1. The sag especially by activation polarization is large, and, as for

this, the permeate lump by the electrode substrate of catalyst coating liquid is considered to be the cause.

[0108] The creation PAN system carbon fiber (Toray Industries make trading card T-300) of an example 2 (1) porosity electric conduction sheet was judged to 12mm and 1mm. Water was made to distribute with vinylon the staple fiber carbon fiber judged to these 12mm. The carbon fiber paper-making object was created by carrying out paper making of these dispersion liquid on a wire gauze.

[0109] Next, it sank into the PFA dispersion (neo chlorofluorocarbon PFA dispersion by Daikin Industries, LTD.) which distributed the staple fiber carbon fiber which cut out this paper-making object to 1mm, and dried. Furthermore, heat treatment was performed at 370 degrees C for 3 hours, and the porosity electric conduction sheet which consists of a PAN system carbon staple fiber (weight ratio 60:40 (12mm and 1mm)) to which PFA adhered 3% of the weight was created. The eyes of this porosity electric conduction sheet were 3 g/m<sup>2</sup>, and thickness was 15 micrometers.

[0110] (2) Catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) 1.25g and i-propanol were added to 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, and the dispersion liquid which stir well and contain catalyst-polymer complex were prepared.

[0111] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the porosity electric conduction sheet created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which a porosity electric conduction sheet and catalyst-polymer complex became integral construction was created. The thickness of 20 micrometers and platinum were attached, amount;0.5 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount;0.2 mg/cm<sup>2</sup>.

[0112] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber spun-yarn textiles (25% of amounts [ ELAT made from E-TEK and PFA attached. ]) which gave a water-repellent finish as electrode substrates, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 120 degrees C, pressure 50MPa).

[0113] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 60 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 650 mW/cm<sup>2</sup>.

[0114] The creation PAN system carbon fiber (Toray Industries make trading card T-300) of an example of comparison 2(1) porosity electric conduction sheet was judged to 12mm and 1mm. Water was made to distribute with vinylon the staple fiber carbon fiber judged to these 12mm. The carbon fiber paper-making object was created by carrying out paper making of these dispersion liquid on a wire gauze.

[0115] Next, it sank into the PFA dispersion (neo chlorofluorocarbon PFA dispersion by Daikin Industries, LTD.) which distributed the staple fiber carbon fiber which cut out this paper-making object to 1mm, and dried. Furthermore, heat treatment was performed at 370 degrees C for 3 hours, and the porosity electric conduction sheet which consists of a PAN system carbon staple fiber (weight ratio 60:40 (12mm and 1mm)) to which PFA adhered 3% of the weight was created. The eyes of this porosity electric conduction sheet were 20 g/m<sup>2</sup>, and thickness was 80 micrometers.

[0116] (2) Catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) 1.25g and i-propanol were added to 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, and the dispersion liquid which stir well and contain catalyst-polymer complex were prepared.

[0117] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the porosity electric conduction sheet created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which a porosity electric conduction sheet and catalyst-polymer complex became integral construction was created. The thickness of 80 micrometers and platinum were attached, amount;0.5 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount;0.2 mg/cm<sup>2</sup>.

[0118] (4) Film-electrode complex was created like the example 2 using two catalyst beds created with the creation above (3) of film-electrode complex (MEA).

[0119] (5) When the polymer electrolyte fuel cell cel was created on both sides of the film-electrode complex created with the fuel cell assessment above (4) to the separator and current-electrical-potential-

difference (I-V) measurement was performed on an example 2 and these conditions, the horsepower output was 350 mW/cm<sup>2</sup> and activation polarization and diffusion polarization of engine performance were greatly poor.

[0120] The creation PAN system carbon fiber (Toray Industries make trading card T-300) of an example 3 (1) porosity electric conduction sheet was judged to 6mm. Water was made to distribute with vinylon the staple fiber carbon fiber judged to these 6mm. The carbon fiber paper-making object was created by carrying out paper making of these dispersion liquid on a wire gauze.

[0121] Next, it sank into the PFA dispersion (neo chlorofluorocarbon PFA dispersion by Daikin Industries, LTD.) which distributed acetylene black (DIN by DENKI KAGAKU KOGYO K.K. a turnip rack) by making this paper-making object into carbon black, and dried. Furthermore, heat treatment was performed at 370 degrees C for 3 hours, and acetylene black created the porosity electric conduction sheet with which PFA consists of a PAN system carbon staple fiber which adhered 10% of the weight 5% of the weight. The eyes of this porosity electric conduction sheet were 3 g/m<sup>2</sup>, and thickness was 13 micrometers.

[0122] (2) Catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;40wt%) 0.78g and ethanol were added to 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, and the dispersion liquid which stir well and contain catalyst-polymer complex were prepared.

[0123] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the porosity electric conduction sheet created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which a porosity electric conduction sheet and catalyst-polymer complex became integral construction was created. The thickness of 15 micrometers and platinum were attached, amount;0.4 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount;0.32 mg/cm<sup>2</sup>.

[0124] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber spun-yarn textiles (25% of amounts [ ELAT made from E-TEK and PFA attached. ]) which gave a water-repellent finish as electrode substrates, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 120 degrees C, pressure 40MPa).

[0125] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 80 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 700 mW/cm<sup>2</sup>.

[0126] It is [ screen coating and ] drying on the electrode substrate (acetylene black adhered 80% of the weight, and 10mg /of PFA(s) adhered 20 % of the weight two times cm) which carried out coating of the carbon black on the carbon fiber spun-yarn textiles electrode which used the dispersion liquid containing the catalyst-polymer complex created in the coating example 3 (2) of the example 3 (1) catalyst bed of a comparison, without adding ethanol in the example 3. The electrode substrate with a catalyst bed (the thickness of 15 micrometers and platinum attached and amount;0.4 mg/cm<sup>2</sup> and Nafion attached amount;0.32 mg/cm<sup>2</sup>) was created.

[0127] (2) Two electrode substrates with a catalyst bed created with creation and the assessment above (1) of film-electrode complex and the proton exchange film used in the example 1 were prepared. The catalyst bed was made to counter the proton exchange film, the laminating of an electrode substrate with a catalyst bed / proton exchange film / the electrode substrate with a catalyst bed was carried out in this order, and film-electrode complex was created by performing a heat press like an example 3.

[0128] An example 3 and these conditions created and estimated the polymer electrolyte fuel cell cel for this film-electrode complex. The horsepower outputs were 400 mW/cm<sup>2</sup> and were the bad engine performance compared with the example 3. The sag by the activation polarization especially accompanying lowering of gaseous diffusion nature is large, and it is considered to be the cause that this carried out coating of the carbon black on the carbon fiber spun-yarn textiles electrode.

[0129] The creation PAN system carbon fiber (Toray Industries make trading card T-300) of an example 4 (1) porosity electric conduction sheet was judged to 3mm and 0.1mm. Water was made to distribute with vinylon the staple fiber carbon fiber judged to these 3mm. The carbon fiber paper-making object was created by carrying out paper making of these dispersion liquid on a wire gauze.

[0130] Next, it sank into the PFA dispersion (neo chlorofluorocarbon PFA dispersion by Daikin Industries, LTD.) which distributed the staple fiber carbon fiber which cut out this paper-making object to 0.1mm, and

dried. Furthermore, heat treatment was performed at 370 degrees C for 2 hours, and the porosity electric conduction sheet which consists of a PAN system carbon staple fiber (weight ratio 80:20 (3mm and 0.1mm)) to which PFA adhered 3% of the weight was created. The eyes of this porosity electric conduction sheet were 5 g/m<sup>2</sup>, and thickness was 15 micrometers.

[0131] (2) The dispersion liquid which stir well catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) 0.63g in 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, and contain catalyst-polymer complex in them were prepared.

[0132] (3) The catalyst bed of the sheet which can be become independent from which the dispersion liquid containing the catalyst-polymer complex created above (2) were dried after coating by screen-stencil, and a porosity electric conduction sheet and catalyst-polymer complex became integral construction on the porosity electric conduction sheet created with the creation above (1) of a catalyst bed was created. The thickness of 20 micrometers and platinum were attached, amount;0.4 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount;0.32 mg/cm<sup>2</sup>.

[0133] (4) The staple fiber and expanded graphite powder (the Toyo Tanso make, bulk density 0.14g/cm<sup>3</sup>, the mean diameter 100, or 200 micrometers) of a PAN system carbon fiber which were cut into creation die length of 12mm of an electrode substrate were mixed to 1:1 by the weight ratio, and it distributed in the sodium carboxymethyl-cellulose water solution. The sheet with which expanded graphite powder adhered to the staple fiber of a carbon fiber was milled on the wire gauze using these dispersion liquid. The filter paper of two sheets was lightly pressurized on both sides of the sheet in order to remove moisture. Then, the filter paper was removed and the sheet was dried. The roll press of the sheet was carried out after desiccation, and the porosity electric conduction sheet was manufactured. The obtained sheets were 80 g/m<sup>2</sup>. After performing 200 degrees C and heat treatment for 30 minutes for this porosity electric conduction sheet in air, it sank in, PFA dispersion (neo chlorofluorocarbon PFA dispersion, Daikin Industries, LTD. make) was inserted into the filter paper of two sheets, and it pressurized and dried lightly.

Furthermore 400 degrees C and heat treatment of 3 hours were performed, pressurizing this sheet by 14.7kPa (0.15 kgf/cm<sup>2</sup>), and the electrode substrate was manufactured. Expanded graphite was attached, as for the amount, PFA was attached 50% of the weight, and the amount was 15 % of the weight.

[0134] (5) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two electrode substrates created with the above (4), and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 130 degrees C, pressure 50MPa).

[0135] (6) On both sides of the film-electrode complex created with the fuel cell assessment above (5), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel -- cel temperature; -- when current-electrical-potential-difference (I-V) measurement was performed in 70 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 500 mW/cm<sup>2</sup>.

[0136] The electrode substrate with a catalyst bed (the thickness of 20 micrometers and platinum attached 0.4mg /of 2 and Nafion(s) attached [ Amount; ] cm amount;0.32 mg/cm<sup>2</sup>) was created screen coating and by drying on the electrode substrate which carried out coating of the carbon black on the porosity electric conduction sheet which created the dispersion liquid containing the catalyst-polymer complex created in the coating example 4 (2) of the example 4 (1) catalyst bed of a comparison in the example 4 (4).

[0137] (2) Two electrode substrates with a catalyst bed created with creation and the assessment above (1) of film-electrode complex and the proton exchange film used in the example 1 were prepared. The catalyst bed was made to counter the proton exchange film, the laminating of an electrode substrate with a catalyst bed / proton exchange film / the electrode substrate with a catalyst bed was carried out in this order, and film-electrode complex was created by performing a heat press like an example 4.

[0138] An example 4 and these conditions created and estimated the polymer electrolyte fuel cell cel for this film-electrode complex. The horsepower outputs were 350 mW/cm<sup>2</sup> and were the bad engine performance compared with the example 4. The sag by the activation polarization especially accompanying lowering of gaseous diffusion nature is large, and it is considered to be the cause that this carried out coating of the carbon black on the carbon fiber spun-yarn textiles electrode.

[0139] After cutting the creation PAN system fire resistance-ized yarn of an example 5(1) porosity electric conduction sheet into the staple fiber and card-izing it, by the water jet punching method, nonwoven fabric processing was carried out and carbonization processing was performed at 1600 degrees C. It sank into the

PTFE dispersion (Pori Flon TFE dispersion by Daikin Industries, LTD.) which distributed carbon black (acetylene black; DIN by DENKYO KAGAKU KOGYO K.K. a turnip rack), and carbon fiber nonwoven fabric was dried. Furthermore, heat treatment was performed at 400 degrees C for 3 hours, and carbon black created the porosity electric conduction sheet which consists of a PAN system carbon staple fiber nonwoven fabric to which PTFE adhered 20% of the weight 10% of the weight. The eyes of this porosity electric conduction sheet were 3 g/m<sup>2</sup>, and thickness was 10 micrometers.

[0140] (2) The dispersion liquid which may add catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) 0.83g to 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, stir, and contain catalyst-polymer complex were prepared.

[0141] (3) The catalyst bed of the sheet which can be become independent from which the dispersion liquid containing the catalyst-polymer complex created above (2) were dried after coating by screen-stencil, and a porosity electric conduction sheet and catalyst-polymer complex became integral construction on the porosity electric conduction sheet created with the creation above (1) of a catalyst bed was created. The thickness of 15 micrometers and platinum were attached, amount;0.4 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount;0.24 mg/cm<sup>2</sup>.

[0142] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber papers (Toray Industries TGP-H -060) which gave a water-repellent finish as an electrode substrate, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 150 degrees C, pressure 50MPa).

[0143] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 80 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 600 mW/cm<sup>2</sup>.

[0144] After cutting the creation PAN system fire resistance-ized yarn of an example 6(1) porosity electric conduction sheet into the staple fiber and card-izing it, nonwoven fabric processing was carried out by the water jet punching method, carbonization processing was performed at 1600 degrees C, and the porosity electric conduction sheet was created. The eyes of this porosity electric conduction sheet were 3 g/m<sup>2</sup>, and thickness was 10 micrometers.

[0145] (2) The dispersion liquid which may add catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) to the creation PTFE dispersion (Pori Flon TFE dispersion by Daikin Industries, LTD.) of catalyst-polymer complex, stir, and contain catalyst-polymer complex were prepared.

[0146] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the porosity electric conduction sheet top created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which a porosity electric conduction sheet and catalyst-polymer complex became integral construction was created. Impregnation and the catalyst bed which dries and contains a proton exchange polymer were created in the Nafion solution made from Aldrich of marketing of this catalyst bed (5 % of the weight). The thickness of 15 micrometers and platinum were attached, amount;0.4 mg/cm<sup>2</sup> and Nafion were attached, amount;0.2mg/cm<sup>2</sup> and PTFE were attached, and this catalyst bed was amount;0.2 mg/cm<sup>2</sup>.

[0147] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber spun-yarn textiles (ELAT made from E-TEK) which gave a water-repellent finish as electrode substrates, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 140 degrees C, pressure 50MPa).

[0148] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 70 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 600 mW/cm<sup>2</sup>.

[0149] After cutting the creation polyphenylene sulfide fiber of an example 7(1) porosity electric conduction sheet into the staple fiber and card-izing it, nonwoven fabric processing was carried out by the

needle punching method, and the non-conductive nonwoven fabric was created. This non-conductive textile was sunk into N-methyl-2-pyrrolidone solution of PVDF which distributed carbon black (acetylene black; DIN by the electrical machinery chemical-industry company a turnip rack), and wet coagulation was performed by being promptly immersed in a methanol. This was dried and the porosity electric conduction sheet to which PVDF adhered 3% of the weight was created. The eyes of this porosity electric conduction sheet were 4 g/m<sup>2</sup>, and thickness was 20 micrometers.

[0150] (2) The dispersion liquid which may add catalyst support carbon (catalyst-t, BlackPearls made from carbon; Cabot, amount of platinum support; 30wt%) 1.0g to 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, stir, and contain catalyst-polymer complex were prepared.

[0151] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the porosity electric conduction sheet created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which a porosity electric conduction sheet and catalyst-polymer complex became integral construction was created. The thickness of 25 micrometers and platinum were attached, amount; 0.4 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount; 0.32 mg/cm<sup>2</sup>.

[0152] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber papers (Toray Industries TGP-H -060) which gave a water-repellent finish as an electrode substrate, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 130 degrees C, pressure 50MPa).

[0153] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 70 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 600 mW/cm<sup>2</sup>.

[0154] After cutting the creation PAN system fire resistance-ized yarn of an example 8(1) porosity electric conduction sheet into the staple fiber and card-izing it, nonwoven fabric processing was carried out by the needle punching method, carbonization processing was performed at 1400 degrees C, and the porosity electric conduction sheet was created. The eyes of this porosity electric conduction sheet were 3 g/m<sup>2</sup>, and thickness was 15 micrometers.

[0155] (2) The Nafion solution made from Aldrich of creation marketing of catalyst-polymer complex (5 % of the weight) was condensed, and it could be 15 % of the weight. The dispersion liquid which may add catalyst support carbon (catalyst ;P. t, VulcanXC made from carbon; Cabot- 72, amount of platinum support; 50wt%) 1.88g to 5g of this solution, stir, and contain catalyst-polymer complex were prepared.

[0156] (3) After impregnation, it sinks into a methanol promptly, and wet coagulation is performed to the dispersion liquid containing the catalyst-polymer complex which created above (2) the porosity electric conduction sheet created with the creation above (1) of a catalyst bed, they were dried, a porosity electric conduction sheet and catalyst-polymer complex became integral construction, and the catalyst bed of the sheet which can be become independent which has fine porous structure was created. The thickness of 25 micrometers and platinum were attached, amount; 0.3 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount; 0.24 mg/cm<sup>2</sup>.

[0157] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber papers (Toray Industries TGP-H -060) which gave a water-repellent finish as an electrode substrate, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 150 degrees C, pressure 50MPa).

[0158] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 80 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 700 mW/cm<sup>2</sup>.

[0159] The creation PTFE fiber (Toray Industries Toyo Flon) of an example 9(1) non-conductive textile was judged to 3mm. The carboxymethyl-cellulose (CMC) water solution was made to distribute this cut-out staple fiber PTFE. The PTFE paper-making object was created by carrying out paper making of these

dispersion liquid on a wire gauze.

[0160] Next, application-of-press heat treatment was performed for paper-making object at 370 degrees C for 3 hours, and the non-conductive textile was created. The eyes of this non-conductive textile were 10 g/m<sup>2</sup>, and thickness was 20 micrometers.

[0161] (2) Catalyst support carbon (catalyst; P. t, VulcanXC made from carbon; Cabot- 72, amount of platinum support; 50wt%) 1.25g and i-propanol were added to 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, and the dispersion liquid which stir well and contain catalyst-polymer complex were prepared.

[0162] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the non-conductive textile created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which a non-conductive textile and catalyst-polymer complex became integral construction was created. The thickness of 20 micrometers and platinum were attached, amount; 0.5 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount; 0.2 mg/cm<sup>2</sup>.

[0163] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber spun-yarn textiles (25% of amounts [ ELAT made from E-TEK and PFA attached. ]) which gave a water-repellent finish as electrode substrates, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 130 degrees C, pressure 50MPa).

[0164] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 60 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 650 mW/cm<sup>2</sup>.

[0165] In the coating example 9 (2) of the example 5 (1) catalyst bed of a comparison, the electrode substrate with a catalyst bed (the thickness of 30 micrometers and platinum attached 0.5mg /of 2 and Nafion(s) attached [ Amount; ] cm amount; 0.2 mg/cm<sup>2</sup>) was created screen coating and by drying on the electrode substrate which used the dispersion liquid containing the catalyst-polymer complex created without adding i-propanol in the example 9.

[0166] (2) Two electrode substrates with a catalyst bed created with creation and the assessment above (1) of film-electrode complex and the proton exchange film used in the example 9 were prepared. The catalyst bed was made to counter the proton exchange film, the laminating of an electrode substrate with a catalyst bed / proton exchange film / the electrode substrate with a catalyst bed was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 130 degrees C, pressure 50MPa) like an example 9.

[0167] An example 1.1 and these conditions created and estimated the polymer electrolyte fuel cell cel for this film-electrode complex. The horsepower outputs were 200 mW/cm<sup>2</sup> and were the bad engine performance compared with the example 9. The sag especially by activation polarization was large, and this judged the creation PFA fiber (Toray Industries Toyo Flon) of the example 10(1) non-conductive textile by which the permeate lump by the electrode substrate of catalyst coating liquid is considered to be the cause to 3mm. The CMC water solution was made to distribute this cut-out staple fiber PFA. The PFA paper-making object was created by carrying out paper making of these dispersion liquid on a wire gauze.

[0168] Next, the non-conductive textile was created by performing heat treatment for this paper-making object at 280 degrees C for 3 hours. By extending this non-conductive textile, as for eyes, 10 g/m<sup>2</sup> was obtained, and, as for thickness, 15 micrometers was obtained.

[0169] (2) Catalyst support carbon (catalyst; P. t, VulcanXC made from carbon; Cabot- 72, amount of platinum support; 50wt%) 1.25g and ethanol were added to 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, and the dispersion liquid which stir well and contain catalyst-polymer complex were prepared.

[0170] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the non-conductive textile created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which a non-conductive textile and catalyst-polymer complex became integral construction was created. The thickness of 15 micrometers and platinum were attached, amount; 0.4 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount; 0.16 mg/cm<sup>2</sup>.

[0171] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex



(MEA), two carbon fiber spun-yarn textiles (25% of amounts [ ELAT made from E-TEK and PFA attached. ]) which gave a water-repellent finish as electrode substrates, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 130 degrees C, pressure 50MPa).

[0172] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 60 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 650 mW/cm<sup>2</sup>.

[0173] The creation FEP fiber (Toray Industries Toyo Flon) of an example of comparison 6(1) porosity electric conduction sheet was judged to 3mm. Water was made to distribute with vinylon the staple fiber PFA cut out to these 3mm. The PFA fiber paper-making object was created by carrying out paper making of these dispersion liquid on a wire gauze.

[0174] Next, heat treatment was performed for this paper-making object at 250 degrees C for 3 hours, and the non-conductive textile was created. The eyes of this porosity electric conduction sheet were 40 g/m<sup>2</sup>, and thickness was 80 micrometers.

[0175] (2) Catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) 1.25g and ethanol were added to 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, and the dispersion liquid which stir well and contain catalyst-polymer complex were prepared.

[0176] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the non-conductive textile created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which a non-conductive textile and catalyst-polymer complex became integral construction was created. The thickness of 80 micrometers and platinum were attached, amount;0.4 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount;0.16 mg/cm<sup>2</sup>.

[0177] (4) Film-electrode complex was created like the example 10 using two catalyst beds created with the creation above (3) of film-electrode complex (MEA).

[0178] (5) When the polymer electrolyte fuel cell cel was created on both sides of the film-electrode complex created with the fuel cell assessment above (4) to the separator and current-electrical-potential-difference (I-V) measurement was performed on an example 10 and these conditions, the horsepower output was 350 mW/cm<sup>2</sup> and activation polarization of engine performance was greatly poor.

[0179] The creation PTFE fiber (Toray Industries Toyo Flon) of an example 11(1) non-conductive textile was judged to 6mm. The CMC water solution was made to distribute the staple fiber PFA cut out to these 6mm. The PFA fiber paper-making object was created by carrying out paper making of these dispersion liquid on a wire gauze.

[0180] Next, it sank into the PFA dispersion (neo chlorofluocarbon PFA dispersion by Daikin Industries, LTD.) which distributed acetylene black (DIN by DENKI KAGAKU KOGYO K.K. a turnip rack) by making this paper-making object into carbon black, and dried. Furthermore, heat treatment was performed at 370 degrees C for 3 hours, and the textile to which carbon black is attached and which an amount becomes from the PTFE staple fiber which is 10 % of the weight was created. By extending this textile, eyes obtained 3 g/m<sup>2</sup> and thickness obtained the 13-micrometer non-conductive textile.

[0181] (2) Catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;40wt%) 0.78g and ethanol were added to 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, and the dispersion liquid which stir well and contain catalyst-polymer complex were prepared.

[0182] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the textile created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which a textile sheet and catalyst-polymer complex became integral construction was created. The thickness of 15 micrometers and platinum were attached, amount;0.4 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount;0.32 mg/cm<sup>2</sup>.

[0183] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber spun-yarn textiles (25% of amounts [ ELAT made from E-TEK and PFA attached. ]) which gave a water-repellent finish as electrode substrates, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode



complex was created by performing a heat press (temperature of 130 degrees C, pressure 50MPa).

[0184] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 80 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 700 mW/cm<sup>2</sup>.

[0185] The creation PTFE fiber (Toray Industries Toyo Flon) of an example 12(1) non-conductive textile was judged to 3mm. The amount of one half of the staple fiber PTFE fiber judged to these 3mm was taken, and the beating PTFE fibrillated by mashing this was obtained. The CMC water solution was made to distribute Beating PTFE for the 3mm staple fiber PTFE, and the PTFE paper-making sheet was created by carrying out paper making of these dispersion liquid on a wire gauze.

[0186] Next, the non-conductive textile which extends at 370 degrees C and consists this paper-making sheet of PTFE after 3-hour heat treatment at them was created. The eyes of this non-conductive textile were 10 g/m<sup>2</sup>, and thickness was 10 micrometers.

[0187] (2) The dispersion liquid which stir well catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) 0.63g in 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, and contain catalyst-polymer complex in them were prepared.

[0188] (3) The catalyst bed of the sheet which can be become independent from which the dispersion liquid containing the catalyst-polymer complex created above (2) were dried after coating by screen-stencil, and a porosity electric conduction sheet and catalyst-polymer complex became integral construction on the porosity electric conduction sheet created with the creation above (1) of a catalyst bed was created. The thickness of 20 micrometers and platinum were attached, amount;0.4 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount;0.32 mg/cm<sup>2</sup>.

[0189] (4) The staple fiber and expanded graphite powder (the Toyo Tanso make, bulk density 0.14g/cm<sup>3</sup>, the mean diameter 100, or 200 micrometers) of a PAN system carbon fiber which were cut into creation die length of 12mm of an electrode substrate were mixed to 1:1 by the weight ratio, and it distributed in the sodium carboxymethyl-cellulose water solution. The sheet with which expanded graphite powder adhered to the staple fiber of a carbon fiber was milled on the wire gauze using these dispersion liquid. The filter paper of two sheets was lightly pressurized on both sides of the sheet in order to remove moisture. Then, the filter paper was removed and the sheet was dried. The roll press of the sheet was carried out after desiccation, and the porosity electric conduction sheet was manufactured. The obtained sheets were 80 g/m<sup>2</sup>. After performing 200 degrees C and heat treatment for 30 minutes for this porosity electric conduction sheet in air, it sank in, PFA dispersion (neo chlorofluorocarbon PFA dispersion, Daikin Industries, LTD. make) was inserted into the filter paper of two sheets, and it pressurized and dried lightly. Furthermore 400 degrees C and heat treatment of 3 hours were performed, pressurizing this sheet by 14.7kPa (0.15 kgf/cm<sup>2</sup>), and the electrode substrate was manufactured. PFA was attached and the amount was 15 % of the weight.

[0190] (5) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two electrode substrates created with the above (4), and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 130 degrees C, pressure 50MPa).

[0191] (6) On both sides of the film-electrode complex created with the fuel cell assessment above (5), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 70 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 500 mW/cm<sup>2</sup>.

[0192] After cutting the creation PAN system fire resistance-ized yarn of an example 13(1) non-conductive textile into the staple fiber and card-izing it, nonwoven fabric processing was carried out by the water jet punching method. The eyes of this fire resistance-ized nonwoven fabric were 10 g/m<sup>2</sup>, and thickness was 20 micrometers.

[0193] (2) The dispersion liquid which may add catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) 0.83g to 5g (5 % of the weight) of Nafion solutions made from Aldrich of creation marketing of catalyst-polymer complex, stir, and contain catalyst-polymer complex were prepared.

[0194] (3) The catalyst bed of the sheet which can be become independent from which the roll press

performed pressure treatment and a non-conductive textile and catalyst-polymer complex became integral construction after coating and impregnation by screen-stencil about the dispersion liquid containing the catalyst-polymer complex created above (2) on the porosity electric conduction sheet created with the creation above (1) of a catalyst bed was created. The thickness of 10 micrometers and platinum were attached, amount; 0.4 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount; 0.24 mg/cm<sup>2</sup>.

[0195] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber papers (Toray Industries TGP-H-060) which gave a water-repellent finish as an electrode substrate, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 130 degrees C, pressure 50MPa).

[0196] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 80 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 600 mW/cm<sup>2</sup>.

[0197] Extending the creation PTFE paper-making object (TOMIFAI lek FP made of \*\*\*\* paper making- 50) of an example 14(1) non-conductive textile, eyes created 5 g/m<sup>2</sup> and thickness created the 15-micrometer non-conductive textile.

[0198] (2) The dispersion liquid which may add catalyst support carbon (catalyst ; P. t, VulcanXC made from carbon; Cabot- 72, amount of platinum support; 50wt%) to the creation PTFE dispersion (Pori Flon TFE dispersion by Daikin Industries, LTD.) of catalyst-polymer complex, stir, and contain catalyst-polymer complex were prepared.

[0199] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the non-conductive textile created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which an unjust conductivity textile and catalyst-polymer complex became integral construction was created. Impregnation and the catalyst bed which dries and contains a proton exchange polymer were created in the Nafion solution made from Aldrich of marketing of this catalyst bed (5 % of the weight). The thickness of 15 micrometers and platinum were attached, amount; 0.4 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount; 0.2 mg/cm<sup>2</sup>.

[0200] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber spun-yarn textiles (ELAT made from E-TEK) which gave a water-repellent finish as electrode substrates, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 130 degrees C, pressure 50MPa).

[0201] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 70 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 600 mW/cm<sup>2</sup>.

[0202] The creation PAN system fire resistance-ized yarn of an example 15(1) non-conductive textile was cut out to 3mm. PFA dispersion (neo chlorofluocarbon dispersion, Daikin Industries, LTD. make) was made to distribute the fire resistance-ized staple fiber cut out to these 3mm. The fire resistance-ized fiber paper-making sheet was created by carrying out paper making of these dispersion liquid on a wire gauze.

[0203] Next, the non-conductive textile which performs a roll press and consists this paper-making sheet of a fire resistance-ized staple fiber after 3-hour heat treatment at 370 degrees C was created. The eyes of this non-conductive textile were 10 g/m<sup>2</sup>, and thickness was 10 micrometers.

[0204] This textile was sunk into N-methyl pyrrolidone solution of PVDF which distributed carbon black (acetylene black; DIN by DENKI KAGAKU KOGYO K.K. a turnip rack), and wet coagulation was performed by being promptly immersed in a methanol. This was dried and carbon black created the porosity electric conduction sheet which consists of a PAN system carbon staple fiber nonwoven fabric to which PVDF adhered 1% of the weight 5% of the weight. The eyes of this porosity electric conduction sheet were 4 g/m<sup>2</sup>, and thickness was 20 micrometers.

[0205] (2) The dispersion liquid which may add catalyst support carbon (catalyst-t, BlackPearls made from carbon; Cabot, amount of platinum support; 30wt%) 1.0g to 5g (5 % of the weight) of Nafion solutions made

from Aldrich of creation marketing of catalyst-polymer complex, stir, and contain catalyst-polymer complex were prepared.

[0206] (3) The dispersion liquid containing the catalyst-polymer complex which created above (2) the non-conductive textile created with the creation above (1) of a catalyst bed were dried after impregnation, and the catalyst bed of the sheet which can be become independent from which a non-conductive textile and catalyst-polymer complex became integral construction was created. The thickness of 25 micrometers and platinum were attached, amount; 0.4 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount; 0.32 mg/cm<sup>2</sup>.

[0207] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber papers (Toray Industries TGP-H -060) which gave a water-repellent finish as an electrode substrate, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 130 degrees C, pressure 50MPa).

[0208] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 70 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 600 mW/cm<sup>2</sup>.

[0209] The creation PTFE fiber (Toray Industries Toyo Flon) of an example 16(1) non-conductive textile was judged to 3mm. The amount of one half of the PTFE staple fiber cut out to these 3mm was mashed and fibrillated, and beating PTFE fiber was obtained. The CMC water solution was made to distribute the staple fiber PTFE and beating PTFE fiber which were judged to 3mm. The PTFE fiber paper-making object was created by carrying out paper making of these dispersion liquid on a wire gauze.

[0210] Next, this paper-making object was extended after 3-hour heat treatment at 370 degrees C, eyes created 10 g/m<sup>2</sup> and thickness created the 10-micrometer non-conductive textile.

[0211] (2) The Nafion solution made from Aldrich of creation marketing of catalyst-polymer complex (5 % of the weight) was condensed, and it could be 15 % of the weight. The dispersion liquid which may add catalyst support carbon (catalyst ; P. t, VulcanXC made from carbon; Cabot- 72, amount of platinum support; 50wt%) 1.88g to 5g of this solution, stir, and contain catalyst-polymer complex were prepared.

[0212] (3) After impregnation, it sinks into a methanol promptly, and wet coagulation is performed to the dispersion liquid containing the catalyst-polymer complex which created above (2) the non-conductive textile created with the creation above (1) of a catalyst bed, they were dried, a non-conductive textile and catalyst-polymer complex became integral construction, and the catalyst bed of the sheet which can be become independent which has fine porous structure was created. The thickness of 25 micrometers and platinum were attached, amount; 0.3 mg/cm<sup>2</sup> and Nafion were attached, and this catalyst bed was amount; 0.24 mg/cm<sup>2</sup>.

[0213] (4) It is Du as two catalyst beds created with the creation above (3) of film-electrode complex (MEA), two carbon fiber papers (Toray Industries TGP-H -060) which gave a water-repellent finish as an electrode substrate, and proton exchange film. Nafion112 made from Pont was prepared. The laminating of an electrode substrate / catalyst bed / proton exchange film / catalyst bed / the electrode substrate was carried out in this order, and film-electrode complex was created by performing a heat press (temperature of 130 degrees C, pressure 50MPa).

[0214] (5) On both sides of the film-electrode complex created with the fuel cell assessment above (4), the polymer electrolyte fuel cell cel was created to the separator. this fuel cell cel — cel temperature; — when current-electrical-potential-difference (I-V) measurement was performed in 80 degrees C, fuel gas; hydrogen, oxidation gas; air, and rate; anode of gas utilization 70%/cathode 40%, the horsepower output was 700 mW/cm<sup>2</sup>.

[0215]

[Effect of the Invention] The electrode which solved the problem of the complicated actuation for solving the problem of the catalyst \*\*\*\* lump in spreading of a up to [ a porosity base material ], and avoiding swelling of the film in spreading on the proton exchange film by the catalyst bed of this invention is obtained, therefore the utilization effectiveness of a catalyst improves, it is the high power engine performance, and the low cost-ized electrode by the amount reduction of catalysts is obtained.

[0216] The electrode of this invention is applied to film-electrode complex (MEA), and also is applied also to usual electrochemistry equipment, especially a polymer electrolyte fuel cell, and is applied also to the mobile and automobile using this fuel cell.

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最終頁に続く

(54) 【発明の名称】 電極触媒層、膜-電極複合体およびそれらの製造方法並びにそれらを用いた燃料電池

## (57) 【要約】

【課題】 電極触媒層を形成する際の塗工性不良による性能低下および煩雑な工程によるコスト増大を抑制し、薄く、触媒利用効率が高く、高出力性能の得られる電極触媒層を提供すること。

【解決手段】 少なくとも電極触媒とポリマから構成される触媒-ポリマ複合体と、多孔質導電シートおよび/または非導電性布帛を有してなる担持層とが一体となった構造を有し、厚さが50 μm以下である電極触媒層。

## 【特許請求の範囲】

【請求項 1】少なくとも電極触媒とポリマから構成される触媒-ポリマ複合体と、多孔質導電シートおよび/または非導電性布帛を有してなる坦持層とが一体となった構造を有し、厚さが  $50\mu\text{m}$  以下である電極触媒層。

【請求項 2】多孔質導電シートが無機導電性繊維を用いた織布構造あるいは不織布構造のものである請求項 1 に記載の電極触媒層。

【請求項 3】非導電性布帛が繊維を用いた織布構造あるいは不織布構造のものである請求項 1 に記載の電極触媒層。

【請求項 4】無機導電性繊維が炭素繊維である請求項 2 に記載の電極触媒層。

【請求項 5】非導電性布帛の繊維がフッ素原子を含有してなる繊維である請求項 3 に記載の電極触媒層。

【請求項 6】触媒-ポリマ複合体が坦持層の空隙中に充填されてなる請求項 1～5 のいずれかに記載の電極触媒層。

【請求項 7】電極触媒層の形態が自立可能なシートである請求項 1～6 のいずれかに記載の電極触媒層。

【請求項 8】電極触媒が、白金、パラジウム、金、ルテニウム、及びイリジウムからなる群から選ばれる一種以上の元素を含む請求項 1～7 のいずれかに記載の電極触媒層。

【請求項 9】電極触媒が触媒を担持したカーボンブラックである請求項 1～8 のいずれかに記載の電極触媒層。

【請求項 10】ポリマがフッ素原子を含有するポリマである請求項 1～9 のいずれかに記載の電極触媒層。

【請求項 11】ポリマがプロトン交換基を有するポリマである請求項 1～10 のいずれかに記載の電極触媒層。

【請求項 12】触媒-ポリマ複合体乃至はその前駆体を含む液体を多孔質導電シートまたは非導電性布帛に含浸あるいは塗工することを特徴とする請求項 1～11 のいずれかに記載の電極触媒層の製造方法。

【請求項 13】請求項 1～11 のいずれかに記載の電極触媒層と、プロトン交換膜と電極基材とから構成される膜-電極複合体。

【請求項 14】プロトン交換膜がフッ素原子含有ポリマを有してなる請求項 13 に記載の膜-電極複合体。

【請求項 15】フッ素原子含有ポリマがスルホン酸基を有するフルオロアルキルエーテル側鎖とフルオロアルキル主鎖を有してなるポリマである請求項 14 に記載の膜-電極複合体。

【請求項 16】電極基材が多孔質導電シートである請求項 13～15 のいずれかに記載の膜-電極複合体。

【請求項 17】多孔質導電シートが無機導電性繊維を用いた織布構造あるいは不織布構造である請求項 16 に記載の膜-電極複合体。

【請求項 18】無機導電性繊維が炭素繊維である請求項 17 に記載の膜-電極複合体。

【請求項 19】請求項 1～11 のいずれかに記載の電極触媒層 2 枚の間にプロトン交換膜を配置し、前記プロトン交換膜を挟持した電極触媒層を電極基材 2 枚の間で挟持させて接合することを特徴とする膜-電極複合体の製造方法。

【請求項 20】請求項 1～11 のいずれかに記載の電極触媒層を用いた電気化学装置。

【請求項 21】請求項 13～18 のいずれかに記載の膜-電極複合体を用いた電気化学装置。

【請求項 22】請求項 1～11 のいずれかに記載の電極触媒層を用いた水電解装置。

【請求項 23】請求項 13～18 のいずれかに記載の膜-電極複合体を用いた水電解装置。

【請求項 24】請求項 1～11 のいずれかに記載の電極触媒層を用いた燃料電池。

【請求項 25】請求項 13～18 のいずれかに記載の膜-電極複合体を用いた燃料電池。

【請求項 26】固体高分子型電解質を用いる請求項 24 または 25 に記載の燃料電池。

【請求項 27】請求項 24 又は 25 に記載の燃料電池を電力供給源とする移動体。

【請求項 28】請求項 24 又は 25 に記載の燃料電池を電力供給源とする自動車。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、燃料電池あるいは種々の電気化学装置に用いられる電極あるいは膜-電極複合体とそれらの製造方法に関するものである。

【0002】

【従来の技術】燃料電池は、低排出物、高エネルギー効率で環境への負担の低い発電装置である。このため、近年の地球環境保護への高まりの中で再び脚光を浴びている。従来の大規模発電施設に比べ比較的小規模の分散型発電施設、自動車や船舶など移動体の発電装置として、将来的にも期待されている発電装置である。

【0003】燃料電池には、用いられる電解質の種類により、固体高分子型、リン酸型、固体酸化物型、熔融炭酸塩型、アルカリ型などの種類がある。なかでも固体高分子型燃料電池は、他の燃料電池に比べて、運転温度が低温で起動時間が短く、高出力が得やすい、小型軽量化が見込める、振動に強いなどの特徴を有し移動体の電力供給源に適している。

【0004】燃料電池は、発電を担う反応の起こるアノードとカソードの電極と、アノードとカソード間のイオン伝導体となる電解質とがそれぞれの間でセパレータで挟まれたセルをユニットとして構成されている。電極は、ガス拡散の促進と集（給）電を行う電極基材（集電体とも云う）と、実際に電気化学反応場となる電極触媒層とから構成されている。たとえば固体高分子型燃料電池のアノード電極では、燃料ガスが触媒表面で反応して

プロトンと電子を生じ、電子は電極基材に伝導し、プロトンは電解質のプロトン交換膜へと伝導する。このため、アノード電極には、ガス拡散性、電子電導性、イオン電導性が良好なことが要求される。一方、カソード電極では、酸化ガスが触媒層表面で、電解質から伝導してきたプロトンと、電極基材から伝導してきた電子とが反応して水を生成する。このため、ガス拡散性、電子電導性、イオン電導性ととも、生成した水を効率よく排出することも必要となる。

【0005】このような点から、電極基材（集電体）には導電性を有しガス透過性の良好な多孔質導電シートが用いられてきた。このような多孔質導電シートは、ガス透過性は良好であるが、そのシート上に電極触媒層を塗工すると空孔内への触媒塗液の浸み込む現象が見られた。浸み込んだ触媒は、プロトン交換膜との距離があるためにプロトン伝導性が低下し、また触媒層の膜厚が厚くなるためにガスの拡散性が不良となる。このため、この触媒浸み込み現象により、有効に利用されない触媒が増すこととなる。燃料電池においては貴金属の触媒が用いられるために、有効に使われない触媒が増すことは電極のコストアップに繋がるものである。特に、固体高分子型燃料電池は自動車用途への期待が高い。自動車用途への適応には、性能と共にコストも重要な因子となる。現在の固体高分子型燃料電池は、低コスト化がなされればより一層の普及が見込まれている。

【0006】このため、触媒浸み込みの少ない電極が求められており、種々の提案がなされていた。例えば、多孔性の電極基材の空隙を炭素粒子で充填する、電極基材表面に触媒浸み込み抑制層を設ける、などの公知例として、特開平10-261421号公報、WO98/27606、特開平7-78617号公報、特表平9-501541号公報、特開平10-92439号公報、特開平10-92440号公報などが開示されている。

【0007】また、多孔性の電極基材に塗布することなく、プロトン交換膜上に電極触媒層を設ける、塗工基材に塗布した後に膜に転写するなどの公知例として、J. Electrochem. Soc., 139, L28 (1992)、Electrochimica Acta, 40, 355 (1995)、J. Appl. Electrochem., 22, 1 (1992) などが開示されている。

【0008】

【発明が解決しようとする課題】上記の提案においては、電極基材への触媒層の浸み込みは抑制されるものの、燃料電池性能に悪影響を及ぼしていた。多孔性の電極基材の空隙を炭素粒子で充填する、電極基材表面に触媒浸み込み抑制層を設けるなどの方法においては、水素、空気、あるいは加湿のための水蒸気などのガス拡散性を阻害することとなり、拡散分極や活性化分極の増大を来し出力低下を招くことになった。

【0009】また、多孔性の電極基材に塗布せずに、プロトン交換膜上に電極触媒層を設ける、あるいは塗工基材に塗布した後に膜に転写するなどの方法においては、触媒塗液によるプロトン交換膜の膨潤を抑える目的で特殊な工程が必要となり、煩雑な工程を有しコストがかかるという問題があった。

【0010】本発明は、上記課題を解決し、高出力性能が発現され、触媒の利用効率が向上し、触媒量低減による低コスト化電極が得られることを目的とする。

【0011】

【課題を解決するための手段】本発明において、上記課題を解決するため下記構成を有する。

【0012】すなわち、本発明の電極触媒層は、少なくとも電極触媒とポリマから構成される触媒-ポリマ複合体と、多孔質導電シートおよび/または非導電性布帛を有してなる坦持層とが一体となった構造を有し、厚さが50μm以下であることを特徴とする。

【0013】

【発明の実施の形態】以下、本発明の好ましい実施の形態を説明する。

【0014】本発明は、少なくとも電極触媒とポリマから構成される触媒-ポリマ複合体と多孔質導電シート及び/又は非導電性布帛よりなる坦持層（以下、単に「坦持層」という）とが一体となった構造を有し、厚さが50μm以下であることを特徴とするものであり、ここで用いられる坦持層、電極触媒、ポリマなどは特に限定されるものではない。

【0015】本発明において、触媒-ポリマ複合体と坦持層が一体となった構造を有していることが特徴である。ここで言う一体となった構造とは、坦持層の表面あるいは空隙内部表面に触媒-ポリマ複合体が存在する状態、あるいは坦持層の空隙中に触媒-ポリマ複合体が充填されている状態、触媒-ポリマ複合体が坦持層を覆っている状態、を指している。また、触媒-ポリマ複合体が厚さ方向に坦持層全体に均一に存在している必要はなく、片面に寄った状態で存在していても構わない。但し、厚さ方向とは垂直の方向、即ち、面方向には均一に存在していることが好ましい。

【0016】坦持層の多孔質導電性シートが後述のように無機導電性繊維から構成されている場合には、触媒-ポリマ複合体が繊維と繊維の隙間に存在している状態、繊維の周りに存在している状態、繊維と繊維の交差点に存在している状態などが、一体となった構造である。

【0017】本発明の電極触媒層は、触媒-ポリマ複合体と坦持層が一体でない場合（つまり坦持層と触媒-ポリマ複合体が別々に離れている状態、坦持層から触媒-ポリマ複合体の層が分割できる状態）とは異なる。一体でない場合は、多孔質導電シートからなる電極基材上に電極触媒層を設けた状態、あるいは電極触媒層を設けたプロトン交換膜を多孔質導電シートからなる電極基材に

接合した状態となり、従来の電極基材-電極触媒層-プロトン交換膜からなる膜-電極複合体(MEA)の形態と同じであるために本発明の実施態様とは異なるものである。

【0018】本発明において、電極触媒層の厚さは50 $\mu\text{m}$ 以下であることが特徴であり、従来のリン酸型燃料電池において100~300 $\mu\text{m}$ の電極基材と触媒-ポリマ複合体が一体となった電極触媒層とは基本的に異なるものである。固体高分子型燃料電池は高出力が得られることが特徴であり、このためには燃料電池の内部抵抗を低くすることが必要であるが、低電流域での活性化分極による電圧の低下、および高電流域での拡散分極による電圧の低下を抑えることも重要である。いずれの分極を抑えるにも電極触媒層の厚さが薄い方が好ましく、この点から、本発明の電極触媒層の厚さが50 $\mu\text{m}$ 以下であることが必要となる。好ましくは30 $\mu\text{m}$ 以下、より好ましくは20 $\mu\text{m}$ 以下である。ただし、後述のように、非導電性布帛をプレスにより薄膜化を行うこと、あるいは触媒-ポリマ複合体と非導電性布帛とを一体化した後にプレスすること、さらには膜-電極複合体作成時に電極基材と電極触媒層とプロトン交換膜とをプレスすること等、幾つかのプレス工程が行われるために、最終的に使用されるときに電極触媒層の厚さが50 $\mu\text{m}$ 以下であることが、本発明の特徴となる。

【0019】本発明において、電極触媒層の厚さは、電極断面の走査型電子顕微鏡(SEM)観察によって確認できる。電極触媒層は金属の電極触媒である場合には、SEMとX線マイクロアナリシス(XMA)を併用(SEM-XMA)することで、電極触媒層の厚さを求めることが可能である。上記のSEMあるいはSEM-XMA以外にも、特に限定されることなくさまざまな手法で電極触媒層の厚みを求めることは可能である。特に電極触媒層の形態が自立可能なシートであるために、通常の厚み計で測定することが可能である。

【0020】本発明の電極触媒層は、触媒-ポリマ複合体が担持層と一体となっていることが特徴であるために、電極触媒層の形態が自立可能なシートであることも好ましい実施態様となる。従来の電極触媒層は、上述のように多孔質導電シートから成る電極基材上に設ける方法、あるいはプロトン交換膜上に設ける方法で作成されていた。このため、電極触媒層はその完成以前から電極基材あるいはプロトン交換膜と一体であった。本発明の電極触媒層は、触媒-ポリマ複合体が担持層と一体となっているために、電極基材あるいはプロトン交換膜から独立して存在し得ることが特徴である。つまり、担持層が心材としての役割を果たしており、この担持層が強度維持することにより本発明の電極触媒層の形態が自立可能なシート、即ち、他のシートと積層や接合されていなくても、独立したシートとしてその形態を保て、自重程度ではその構成要素が分離・分解しないシートとなるも

のである。ただし、本発明の電極触媒層が種々の電気化学装置に適用される際には、電極基材やプロトン交換膜と接合されて膜-電極複合体(MEA)となっており、このMEAの状態では電極触媒層はもはやその形態が自立シートであるかの区別は困難である。

【0021】本発明に用いられる担持層としては、電気抵抗が低く、かつ気体が透過しやすい貫通の空隙を有する構造であれば特に限定されることなく用いることが可能である。担持層の多孔質導電シートの構成材としては、たとえば、導電性無機物質を主とするものが挙げられ、この導電性無機物質としては、ポリアクリロニトリルからの焼成体、ピッチからの焼成体、黒鉛及び膨張黒鉛などの炭素材、ステンレススチール、モリブデン、チタンなどが例示される。導電性無機物質の形態は繊維状あるいは粒子状など特に限定されないが、燃料電池などのように電極活物質に気体を用いる電気化学装置に用いる場合、ガス透過性の点から繊維状導電性無機物質(無機導電性繊維)特に炭素繊維が好ましい。担持層に関して、無機導電性繊維を用いた多孔質導電シートとしては、織布あるいは不織布いずれの構造も使用可能である。織布としては、平織、斜織、朱子織、紋織、綴織など特に限定されることなく用いられる。また、不織布としては、抄紙法、ニードルパンチ法、スパンボンド法、ウォータージェットパンチ法、メルトブロー法など特に限定されることなく用いられる。また編物であっても構わない。これらの布帛において、特に炭素繊維を用いた場合、耐炭化紡績糸を用いた平織物を炭化あるいは黒鉛化した織布、耐炭化糸をニードルパンチ法やウォータージェットパンチ法などによる不織布加工した後に炭化あるいは黒鉛化した不織布、耐炭化糸あるいは炭化糸あるいは黒鉛化糸を用いた抄紙法によるマット不織布などが好ましく用いられる。特に薄く強度のある布帛が得られる点から不織布が好ましい。

【0022】担持層の多孔質導電シートの目付としては、無機導電性繊維特に炭素繊維から作られている場合においては1~30 $\text{g}/\text{m}^2$ であるのが好ましい。1 $\text{g}/\text{m}^2$ 未満では多孔質導電シートの強度が低くなる。30 $\text{g}/\text{m}^2$ を超える多孔質導電シートが厚くなり電極触媒層としての性能が低下する。

【0023】担持層の多孔質導電シートの電気抵抗は、シート厚み方向の面積抵抗として50 $\Omega \cdot \text{cm}^2$ 以下であることが好ましい。より好ましくは1 $\Omega \cdot \text{cm}^2$ 以下、さらにより好ましくは100 $\text{m}\Omega \cdot \text{cm}^2$ 以下である。抵抗が高い場合、特に多孔質導電シートが厚いときには電極触媒層における性能が低下する。

【0024】担持層の多孔質導電シートの電気抵抗Rの測定は、次の方法で行う。幅50mm、長さ200mm、厚み1.5mmの表面が平滑な平面を有するガラス状炭素板の片面に、幅50mm、長さ200mm、厚み0.1mmの銅箔が貼着した試験電極板を2枚用意す



る。2枚の試験電極板を、実質的に均一な間隔を保ち、ガラス状炭素板の面同士が対向させる。2枚の試験電極板の、それぞれ的一端に電流用の端子を、それぞれ他端に電圧用の端子を設ける。直径4.6mmの円形に切り出した多孔質導電シートを前記間隙に挿入し、2枚の試験電極板の中央部に載置する。載置したシートに0.98MPaの圧力を作用させるように試験電極板が移動する。電流用の端子から2枚の試験電極板間に1Aの電流を流す。電圧用の端子にて、この時の電圧V(V)を測定する。測定された電圧Vの値から、次式により抵抗R

$$R = V \times 2.3 \times 2.3 \times \pi \times 1000$$

ここで、 $\pi$ は円周率である。

【0025】 担持層の多孔質導電シートとして、炭素繊維からなる無機導電性繊維を用いている場合、炭素繊維としては、ポリアクリロニトリル(PAN)系炭素繊維、フェノール系炭素繊維、ピッチ系炭素繊維、レーヨン系炭素繊維などが例示される。なかでも、PAN系炭素繊維が好ましい。PAN系炭素繊維はピッチ系炭素繊維にくらべて圧縮強さ、引張破断伸度が大きく、折れにくい。このことは、炭素繊維を構成する炭素の結晶化の相異によると考えられる。折れにくい炭素繊維を得るためには、炭素繊維の熱処理温度は2,500℃以下が好ましく、2,000℃以下がより好ましい。

【0026】 担持層の多孔質導電シートに用いられる無機導電性繊維の直径は、20 $\mu$ m以下であるのが好ましい。より好ましいのは12 $\mu$ m以下、さらに好ましいのは8 $\mu$ m以下である。繊維径が太いと多孔質導電シートの厚みが厚くなり、電極性能が低下する。

【0027】 担持層の多孔質導電シートは、水の滞留によるガス拡散・透過性の低下を防ぐために行う撥水処理、水の排出路を形成するための部分的撥水、親水処理や、抵抗を下げるために行われる炭素粉末の添加等を行うことも好ましい実施態様である。

【0028】 本発明の担持層に用いられる非導電性布帛としては、気体が透過しやすい貫通の空隙を有する構造であれば特に限定されることがなく用いることが可能である。非導電性布帛の構成材としては、たとえば、非導電性繊維であれば特に限定されることがなく用いられる。

【0029】 担持層の非導電性布帛を構成する非導電性繊維としては、ポリテトラフルオロエチレン(PTFE)、テトラフルオロエチレン-ヘキサフルオロエチレン共重合体(FEP)、テトラフルオロエチレン-パーフルオロアルキルビニルエーテル共重合体(PFA)、テトラフルオロエチレン-エチレン共重合体(ETFE)、ポリフッ化ビニリデン(PVDF)、ポリフッ化ビニル(PVF)、ポリクロトリフルオロエチレン(CTFE)、塩素化ポリエチレン、耐炎化ポリアクリロニトリル、ポリアクリロニトリル、ポリエステル、ポリアミド、ポリエチレン、ポリプロピレンなど特に限定

されることなく使用可能である。これらの非導電性繊維の中でも、PTFE、FEP、PFA、ETFE、PVDF、PVF、CTFEなどのフッ素原子含有ポリマからなる繊維が、電極反応時の耐食性などの点から好ましいものである。

【0030】 担持層の非導電性布帛としては織布あるいは不織布いずれの構造も使用可能である。織布としては、平織、斜文織、朱子織、紋織、綴織など特に限定されることがなく用いられる。また、不織布としては、抄紙法、ニードルパンチ法、スパンボンド法、ウォータージェットパンチ法、メルトブロー法など特に限定されることがなく用いられる。また編物であっても構わない。これらの布帛において、特に平織物、ニードルパンチ法やウォータージェットパンチ法などによる不織布、抄紙法によるマット不織布などが好ましく用いられる。特に多孔質で薄く強度のある布帛が得られる点から不織布が好ましい。

【0031】 本発明の特徴は、触媒-ポリマ複合体が担持層(ここでは非導電性布帛)と一体となっていることが特徴であり、従来の非導電性の延伸多孔質PTFEの空隙中に電極触媒と高分子固体電解質を充填した構造とは異なるものである。特に非導電性布帛は、延伸多孔質PTFEに比べて触媒-ポリマ複合体の保持性能が高い。このため延伸多孔質PTFEへの触媒塗布および乾燥が複数回必要であるのに対し、より少ない塗布あるいは含浸工程で済む。また、延伸多孔PTFEがフィルム状であるのに対して、本発明では布帛であるために取り扱い性が良好であり作業性に優れるという特徴を有する。

【0032】 担持層の非導電性布帛の厚さは、電極触媒層の厚さと同様に50 $\mu$ m以下であることが好ましい。また、プレスなどによって非導電性布帛作成時の厚さから薄膜化が可能である。

【0033】 担持層の非導電性布帛の目付としては、無機導電性繊維特に炭素繊維から作られている場合においては1~60g/m<sup>2</sup>であるのが好ましい。1g/m<sup>2</sup>未満では多孔質導電シートの強度が低くなる。60g/m<sup>2</sup>を超える多孔質導電シートが厚くなり電極触媒層としての性能が低下する。

【0034】 担持層の非導電性布帛に用いられる非導電性繊維の直径は、30 $\mu$ m以下であるのが好ましい。より好ましいのは20 $\mu$ m以下、さらに好ましいのは10 $\mu$ m以下である。繊維径が太いと多孔質導電シートの厚みが厚くなり、電極性能が低下する。ただし、上述のように、非導電性布帛をプレスすることも薄膜化の点から好ましいものであり、プレス前の繊維径は特に限定されない。

【0035】 担持層の非導電性布帛は、水の滞留によるガス拡散・透過性の低下を防ぐために行う撥水処理、水の排出路を形成するための部分的撥水、親水処理や、抵

抗を下げるために行われる無機導電性粉末の添加等を行うことも好ましい実施態様である。

【0036】 坦持層の多孔質導電シートは、上述のように無機導電性繊維からなる場合、密度の向上、電気抵抗の低減などの点から、導電性粒子、特に導電性無機粒子を含むことも好ましい実施態様である。このような導電性無機粒子としては、電気抵抗や耐食性の点から炭素材、特に炭素粒子が好ましい。

【0037】 このような導電性無機粒子としては、例えば、カーボンブラック粉末、黒鉛粉末、膨張黒鉛粉末、金属粉末、セラミックス粉末などを含んでも良いが、電子導電性と耐触性の点から、カーボンブラック、黒鉛質や炭素質の炭素材が好ましく挙げられる。このような炭素材としては、オイルファーネスブラック、チャンネルブラック、ランプブラック、サーマルブラック、アセチレンブラックなどのカーボンブラックが、電子導電性と比表面積の大きさから好ましいものである。オイルファーネスブラックとしては、キャボット社製バルカンXC-72、バルカンP、ブラックパールズ880、ブラックパールズ1100、ブラックパールズ1300、ブラックパールズ2000、リーガル400、ライオン社製ケッチェンブラックEC、三菱化学社製#3150、#3250などが挙げられ、アセチレンブラックとしては電気化学工業社製デンカブラックなどが挙げられる。またカーボンブラックのほか、天然の黒鉛、ピッチ、コークス、ポリアクリロニトリル、フェノール樹脂、フラン樹脂などの有機化合物から得られる人工黒鉛や炭素などがある。また、これら炭素材を後処理加工した炭素材も用いることが可能である。このような炭素材の中でも、特に、キャボット社製のバルカンXC-72、電気化学工業社製のデンカブラック、ライオン社製のケッチェンブラックなどが電子導電性の点から好ましく用いられる。

【0038】 なお、坦持層に対する導電性粒子の添加量としては、要求される電極特性や用いられる物質の比表面積や電子抵抗などに応じて適宜決められるべきものであり特に限定されない。

【0039】 坦持層（特に主として多孔質導電シートを有してなる場合）は、上記の導電性粒子のほか、高分子物質を添加することも可能である。これにより圧縮や引張りに強くなり、強度、ハンドリング性を高め、無機導電性物質が坦持層から外れたり、坦持層の厚み方向を向くのを防止できる。特に、無機導電性短繊維を抄紙して坦持層を作成する際には、高分子物質を結着剤として用いることは重要である。高分子物質を結着させる方法としては、無機導電性物質を実質的に二次元平面内において無作為な方向に配向させるときに繊維状、粒状、液状の高分子物質を混合する方法と、無機導電性物質が実質的に二次元平面内において無作為な方向に配向された集合体に繊維状、液状の高分子物質を付着させる方法等がある。

【0040】 坦持層の無機導電性物質を結着する高分子物質としては、特に限定されるものではないが電極性能の点からフッ素原子を含有する高分子物質が好ましく用いられる。特にポリテトラフルオロエチレン（PTFE）、テトラフルオロエチレン-ヘキサフルオロプロピレン共重合体（FEP）、テトラフルオロエチレン-パーフルオロアルキルビニルエーテル共重合体（PFA）などが好ましく用いられる。

【0041】 上記のような高分子物質の坦持層としての多孔質導電シートに対する含有率は、0.1～50重量%の範囲にあるのが好ましい。多孔質導電シートの電気抵抗を低くするためには、高分子物質の含有率は少ないほうがよいが、0.1重量%未満ではハンドリングに耐える強度が不足し、無機導電性物質の脱落も多くなる。逆に、40重量%を超えると多孔質導電シートの電気抵抗が増えてくるという問題が生じる。より好ましくは、10～30重量%の範囲である。

【0042】 坦持層の多孔質導電シートに添加した高分子物質は、200℃以上で焼成することも好ましい実施態様である。撥水处理に用いられる上記のフッ素樹脂は、融点以上に加熱することで、撥水性と結着性が向上する。また、フッ素樹脂以外的高分子物質においても、焼成により結着力が向上するほか、電気抵抗の低下、耐食性の向上が見られる。

【0043】 坦持層の多孔質導電シートは、上記の炭素繊維などの無機導電性繊維から構成されるほかに、繊維を用いずに導電性粒子のみとポリマを用いて構成されるものでも構わない。このような導電性粒子としては上述のようにカーボンブラックや黒鉛などの炭素粒子が好ましく用いられる。またポリマとしては、上述のようにフッ素原子を含有するものが好ましく用いられる。導電性粒子とポリマの比率は特に限定されるものではない。

【0044】 坦持層の非導電性布帛は、上記の導電性粒子のほか、高分子物質を添加することも可能である。これにより圧縮や引張りに強くなり、強度、ハンドリング性を高め、無機導電性物質が非導電性布帛から外れるのを防止できる。

【0045】 上記のような高分子物質の非導電性布帛に対する含有率は、0.1～50重量%の範囲にあるのが好ましい。非導電性布帛の電気抵抗を低くするためには、高分子物質の含有率は少ないほうがよいが、0.1重量%未満ではハンドリングに耐える強度が不足し、無機導電性物質の脱落も多くなる。より好ましくは、10～30重量%の範囲である。

【0046】 坦持層の非導電性布帛は、熱処理、延伸、プレスなどの後処理を行うことも好ましい実施態様である。これらの後処理により、薄膜化、空隙率増加、強度増加などの好ましい効果が期待できる。

【0047】 本発明の触媒-ポリマ複合体を構成する電極触媒は、特に限定されることなく公知のものを利用す

ることが可能である。本発明の電極触媒層を燃料電池に用いる場合には、特に限定されるものではないが、白金、パラジウム、金、ルテニウム、イリジウムなどの貴金属触媒が好ましく用いられる。また、これらの貴金属触媒の合金、混合物など、2種以上の元素が含まれていても構わない。

【0048】本発明の電極触媒は、電子伝導性を付与し効率よく分散する目的で、導電性粒子に担持された状態で使用されることも好ましい実施態様である。電極触媒を担持する導電性粒子としては、カーボンブラックなどの炭素材が好ましい。このような炭素材としては、オイルファーネスブラック、チャンネルブラック、ランプブラック、サーマルブラック、アセチレンブラックなどのカーボンブラックが、電子伝導性と比表面積の大きさから好ましいものである。オイルファーネスブラックとしては、キャボット社製バルカンXC-72、バルカンP、ブラックパールズ880、ブラックパールズ1100、ブラックパールズ1300、ブラックパールズ2000、リーガル400、ライオン社製ケッチェンブラックEC、三菱化学社製#3150、#3250などが挙げられ、アセチレンブラックとしては電気化学工業社製デンカブラックなどが挙げられる。またカーボンブラックのほか、天然の黒鉛、ビッチ、コークス、ポリアクリロニトリル、フェノール樹脂、フラン樹脂などの有機化合物から得られる人工黒鉛や炭素などがある。これらの炭素材の形態としては、粒子状のほか繊維状も用いることができる。また、これら炭素材を後処理加工した炭素材も用いることが可能である。このような炭素材の中でも、特に、キャボット社製のバルカンXC-72が電子伝導性の点から好ましく用いられる。導電性粒子に対する電極触媒の担持量は、5〜80重量%が好ましく、20〜60%が特に好ましい。担持量が少ない場合には電極触媒層が高高く厚くなり、多い場合には触媒-ポリマ複合体の分散性が不良となることにより電極性能が低下するので好ましくない。

【0049】本発明の触媒-ポリマ複合体に含まれるポリマとしては、求められる電極性能に応じて適宜選択され、特に限定されるものではないが、フッ素原子を含有するポリマが好ましい。このようなフッ素原子含有ポリマとしては、ポリテトラフルオロエチレン(PTFE)、テトラフルオロエチレン-ヘキサフルオロプロピレン共重合体(FEP)、テトラフルオロエチレン-パーフルオロアルキルビニルエーテル共重合体(PFA)、ポリフッ化ビニリデン(PVDF)、ポリフッ化ビニル(PVF)など、あるいはこれらの共重合体、これらモノマ単位とエチレンやスチレンなどの他のモノマとの共重合体、さらには、ブレンドなども用いることができる。

【0050】また、本発明の触媒-ポリマ複合体に含まれるポリマとしてプロトン交換基を有するポリマがさら

に好ましく用いられる。プロトン交換基としては、スルホン酸基、カルボン酸基、リン酸基などが好適であり好ましく用いられる。なかでも、フルオロアルキルエーテル側鎖とフルオロアルキル主鎖とから構成されるプロトン交換基を有するポリマが最も好ましく用いられる。たとえば、DuPont社製のNafion、旭化成社製のAciplex、旭硝子社製Flemionなどが好ましい。これらのプロトン交換基含有ポリマを溶液または分散液の状態で電極触媒と混合することにより触媒-ポリマ複合体が構成される。この際に、プロトン交換基含有ポリマを溶解あるいは分散化する溶媒は特に限定されるものではないが、プロトン交換基含有ポリマの溶解性の点から極性溶媒が好ましい。プロトン交換基を有する上述のフッ素原子を含むポリマや、エチレンやスチレンなどの他のポリマ、これらの共重合体やブレンドであっても構わない。

【0051】触媒-ポリマ複合体における電極触媒とポリマの比率は、要求される電極特性や用いられるプロトン交換基含有ポリマのイオン電導度などに応じて適宜決められるべきものであり、特に限定されるものではないが、重量比で1〜80%が好ましく、5〜50%がさらに好ましい。ポリマが少ない場合は触媒-ポリマ複合体と担持層が一体となる構造が弱くなることや、イオン伝導度が低くなり、また、多い場合はガス透過性を阻害する点で、いずれも電極性能を低下させる。

【0052】本発明の触媒-ポリマ複合体には、上述の電極触媒、電極触媒担持カーボン、あるいはポリマなどのほかに、種々の物質を添加することも好ましいものである。特に、電子伝導性向上の点から、導電剤を加えることも好ましい実施態様となる。このような導電剤としては、特に限定されるものではないが、上述のカーボンブラックなどの炭素粒子が好ましく用いられる。これら導電剤の添加量としては、要求される電極特性や用いられる物質の比表面積や電子抵抗などに応じて適宜決められるべきものであるが、電極触媒層中の重量比率として1〜80%が好ましく、10〜30%がさらに好ましい。電子伝導体は、少ない場合は電子抵抗が低くなり、多い場合はガス透過性を阻害するほか触媒利用率が低下するなど、いずれも電極性能を低下させる。

【0053】本発明の電極触媒層中に含まれる触媒-ポリマ複合体が、三次元網目微多孔質構造を有することも好ましい実施態様である。なお、「三次元網目微多孔構造」とは、触媒-ポリマ複合体が立体的に繋がった三次元状の網目構造を有している状態をいう。

【0054】電極触媒層に含まれる触媒-ポリマ複合体が三次元網目微多孔質構造を有している場合、その微多孔径が0.05〜5 $\mu$ mであることが好ましい。より好ましくは、0.1〜1 $\mu$ mである。微多孔径は、走査型電子顕微鏡(SEM)などで、表面を撮影した写真から、20個以上好ましくは100個以上の平均から求め

ることができ、通常は100個で測定できる。湿式凝固法によって製造された場合の本発明の微多孔質構造の触媒層は、微多孔径の分布が広いのでできるだけ多くの孔径の平均をとることが好ましい。

【0055】三次元網目微多孔質構造の空孔率は、10～95%であることが好ましい。より好ましくは50～90%である。空孔率は、触媒層全体積から多孔質導電シートの占める体積を減じた残りの体積 ( $V_1$ ) から、さらに触媒-ポリマ複合体の占める体積 ( $V_2$ ) を減じたものを  $V_1$  で除した百分率 (%) ( $= (V_1 - V_2) / V_1 \times 100$ ) である。

【0056】電極触媒層に含まれる触媒-ポリマ複合体は、特に湿式凝固法により作成された三次元網目微多孔質構造のものは、空孔率が大きくガス拡散性や生成水の排出が良好であり、かつ電子伝導性やプロトン伝導性も良好である。従来の多孔化では、触媒粒子径や添加ポリマの粒子径を増大させる、あるいは造孔剤を用いて空孔を形成させるなどが行われているが、このような多孔化方式では触媒担持カーボン間やプロトン交換樹脂間の接触抵抗が電極触媒層に比べて大きくなってしまふ。それ

に対して、湿式凝固法による三次元網目微多孔質構造では、触媒担持カーボンを含んだポリマ複合体が三次元網目状になっているので、このポリマ複合体を電子やプロトンが伝導しやすく、さらに微多孔質構造のためガス拡散性や生成水の排出も良好な構造となっている。

【0057】電極触媒層に含まれる触媒-ポリマ複合体が三次元微多孔質構造を有している場合においても、触媒や電子伝導体、プロトン伝導体に用いられる物質は従来と同様の物質を用いることが可能である。ただし、三次元網目微多孔質構造を有する電極触媒層を作成する際に湿式凝固法によることが好ましい。従って、前記の場合、この湿式凝固法に適したポリマを用いることが好ましく、また、触媒粒子を良く分散し、燃料電池内の酸化-還元雰囲気下で劣化しないポリマを用いることが好ましい。このようなポリマとしては、フッ素原子を含有するポリマが挙げられ、特に限定されるものではないが、たとえば、フルオロアルキルエーテル側鎖とフルオロアルキル主鎖とから構成されるプロトン交換基を有するポリマが最も好ましく用いられ、その他にはポリフッ化ビニル (PVF)、ポリフッ化ビニリデン (PVDF)、ポリヘキサフルオロプロピレン (FEP)、ポリパーフルオロアルキルビニルエーテル (PFA) など、あるいはこれらの共重合体、これらモノマ単位とエチレンやスチレンなどの他のモノマとの共重合体 (例えば、ヘキサフルオロプロピレン-フッ化ビニリデン共重合体)、さらには、ブレンドなども用いることができる。

【0058】この中でも、フルオロアルキルエーテル側鎖とフルオロアルキル主鎖とから構成されるプロトン交換基を有するポリマが最も好ましく、Du Pont社製 Nafion、旭化成社製 Aciplex、旭硝子社

製 Flemionなどを良溶媒 (溶解溶媒) としてアルコール、水やその他の極性溶媒に溶かしたものであるいは分散したものが好ましく用いられる。これらの溶液に電極触媒を加えて良く混練し、貧溶媒 (凝固溶媒) と接触させることで湿式凝固を行い、三次元微多孔質構造を有する触媒-ポリマ複合体が作成される。良溶媒としては、水、メタノール、エタノール、i-プロパノール、N-メチル-2-ピロリドン、N,N-ジメチルスルフォキシド、ジメチルイミダゾリジノンなどの極性溶媒が挙げられ、貧溶媒としては、酢酸ブチル、酢酸エチル、酢酸イソブチル、プロピオン酸メチル、プロピオン酸エチル、ジメチルカーボネート、ジエチルカーボネート、メチルエチルカーボネートなどのエステル類、テトラヒドロフラン、ジオキサンなどの環状エーテル類、などの低誘電率溶媒が挙げられるが、これらに限定されるものではない。

【0059】また、触媒-ポリマ複合体のポリマとして、ポリフッ化ビニリデン (PVDF)、ヘキサフルオロプロピレン-フッ化ビニリデン共重合体などを用いる場合には、良溶媒としてN-メチル-2-ピロリドン、N,N-ジメチルスルフォキシド、ジメチルイミダゾリジノン、ジメチルスルフォキシドなどの非プロトン性極性溶媒が挙げられ、水、メタノール、エタノール、i-プロパノールなどのプロトン性極性溶媒を凝固溶媒とする湿式凝固法を行う。これらのポリマを用いた場合には、電極触媒層内のプロトン伝導性向上のために、上述のプロトン伝導体を添加することが好ましい。

【0060】触媒-ポリマ複合体に用いられるポリマは、上記のフッ素原子を含有するポリマやプロトン交換基を含むポリマを共重合あるいはブレンドして用いることも好ましいものである。特にポリフッ化ビニリデン、ポリ (ヘキサフルオロプロピレン-フッ化ビニリデン)、共重合体などと、プロトン交換基にフルオロアルキルエーテル側鎖とフルオロアルキル主鎖を有するNafionなどのポリマを、ブレンドすることは電極性能の点から好ましいものである。

【0061】触媒-ポリマ複合体の主たる成分は好適には触媒担持カーボンとポリマであり、それらの比率は必要とされる電極特性に応じて適宜決められるべきであり、特に限定されるものではないが、触媒担持カーボン/ポリマの重量比率で5/95～95/5が好ましく用いられる。特に固体高分子型燃料電池用電極触媒層として用いる場合には、触媒担持カーボン/ポリマ重量比率で40/60～85/15が好ましいものである。

【0062】触媒-ポリマ複合体を担持層と一体化させる方法としては、特に限定されるものではないが、含浸法、塗布法などが好ましい方法である。含浸法は、触媒-ポリマ複合体乃至はその前駆体が含まれる液体中に担持層を浸漬し、担持層の空隙中に触媒-ポリマ複合体を浸み込ませることにより行われる。なお、触媒-ポリマ

複合体の前駆体とは、電極触媒層乃至は燃料電池電極の形成が完了するまでには、当該複合体を形成し得るような材料等であり、例えば、触媒とポリマの混合溶液、触媒とポリマの単量体の混合物などが例示できるが特に限定されるものではない。塗布法は、担持層上に触媒-ポリマ複合体が含まれる液体を塗工すること等により行われる。塗工方法については、特に限定されるべきものではないが、ナイフコーター、バーコーター、スプレー、ディップコーター、スピンコーター、ロールコーター、ダイコーター、カーテンコーター、刷毛塗りなどの一般的な塗布方法が用いられる。含浸法、塗布法のいずれの場合においても、触媒-ポリマ複合体が含まれる液体の溶媒、粘度、固形分などは、担持層の空隙率や構成する物質の表面状態などにより適宜選択されるものであり、特に限定され得るものではない。

【0063】本発明の電極触媒層は、プロトン交換膜と電極基材と共に膜-電極複合体 (MEA: Membrane Electrode Assembly) を構成することも本発明の好ましい実施態様である。

【0064】本発明の膜-電極複合体に用いられるプロトン交換膜は特に限定されるものではないが、フッ素原子含有のポリマが、電極内の酸化-還元雰囲気での耐久性という観点から好ましい。また、プロトン交換膜のプロトン交換基としては、スルホン酸基、カルボン酸基、リン酸基など特に限定されるものではない。

【0065】このプロトン交換膜は、上記のプロトン交換基、特にスルホン酸基を有する、スチレン-ジビニルベンゼン共重合体などの炭化水素系と、フッ素原子含有ポリマ、特にフルオロアルキルエーテル側鎖とフルオロアルキル主鎖とから構成される共重合体のパーフルオロ系に大別され、燃料電池が用いられる用途や環境に応じて適宜選択されるべきものであるが、フッ素原子含有ポリマ、特にパーフルオロ系が燃料電池寿命の点から好ましいものである。また、部分的にフッ素原子置換した部分フッ素膜も好ましく用いられる。パーフルオロ膜では、DuPont社製Nafion、旭化成製Aciplex、旭硝子製Flemion、ジャパンゴアテックス社製Goa-selectなどが例示され、部分フッ素膜では、トリフルオロスチレンスルホン酸の重合体やポリフッ化ビニリデンにスルホン酸基を導入したものなどがある。また、プロトン交換膜は1種のポリマばかりでなく、2種以上のポリマの共重合体やブレンドポリマ、2種以上の膜を貼り合わせた複合膜、プロトン交換膜を不織布や多孔フィルムなどで補強した膜なども用いることができる。

【0066】本発明の膜-電極複合体に用いられる電極基材としては、電気抵抗が低く、集(給)電を行えるものであればとくに限定されることなく用いることが可能であるが、特に多孔質導電シートにおいて本発明の特徴が発現されるものである。電極基材に用いられる導電性多孔質シートは、前述の電極触媒層に用いられる多孔質

導電シートと何ら異なることなく適用可能である。ただし、電極触媒層に用いられる多孔質導電シートの厚さが $50\mu\text{m}$ 以下であるのに対し、電極基材に用いられる多孔質導電シートの厚さは $50\sim 400\mu\text{m}$ が好ましく用いられるものである。電極基材に用いられる導電性多孔質シートは、ガス透過性が良好であり電気抵抗の低いシートであれば特に限定されることなく用いることが可能である。

【0067】電極基材の構成材としては、たとえば、導電性無機物質を主とするものが挙げられ、この導電性無機物質としては、ポリアクリロニトリルからの焼成体、ピッチからの焼成体、黒鉛及び膨張黒鉛などの炭素材、ステンレススチール、モリブデン、チタンなどが例示される。導電性無機物質の形態は繊維状あるいは粒子状など特に限定されないが、燃料電池などのように電極活物質に気体を用いる電気化学装置に用いる場合、ガス透過性の点から繊維状導電性無機物質(無機導電性繊維)特に炭素繊維が好ましい。無機導電性繊維を用いた多孔質導電シートとしては、織布あるいは不織布いずれの構造も使用可能である。たとえば、東レ(株)製カーボンペーパーTGPシリーズ、SOシリーズ、E-TEK社製カーボクロスなどが用いられる。

【0068】本発明に用いられる電極基材としては、厚み方向に $2.9\text{MPa}$ の様な面圧を加えたときの厚みが $0.05\sim 0.4\text{mm}$ であるものが好ましい。より好ましくは $0.08\sim 0.2\text{mm}$ である。 $0.05\text{mm}$ より薄い場合、燃料電池に用いる際にセパレータのガス流路に電極基材が埋没し、面方向への拡散・透過性が低くなり、強度が弱く作業性に乏しくなる。 $0.4\text{mm}$ よりも厚い場合、厚み方向の電気抵抗が増えてくる。なお、厚みは、電極基材を均一な厚みで平滑な表面を有する2枚のガラス状炭素板で挟み、 $2.9\text{MPa}$ の様な面圧で加圧し、電極基材を挟まないときと挟んだときのガラス状炭素板の間隔の差から求める。

【0069】電極基材の目付としては $10\sim 220\text{g}/\text{m}^2$ であるのが好ましい。より好ましくは $20\sim 120\text{g}/\text{m}^2$ である。 $10\text{g}/\text{m}^2$ 未満では電極基材の強度が低くなる。また、高分子電解質膜、触媒層、電極基材の一体化時や電池に組んだときに電極基材が薄くなり面方向への拡散・透過効果が不十分になる。 $220\text{g}/\text{m}^2$ を超えると電池に組んだ時に電極基材が厚くなり抵抗が大きくなる。

【0070】電極基材の密度は、厚み方向に $2.9\text{MPa}$ の様な面圧を加えたときに $0.3\sim 0.8\text{g}/\text{cm}^3$ であるのが好ましい。より好ましいのは $0.35\sim 0.7\text{g}/\text{cm}^3$ であり、さらに好ましいのは $0.4\sim 0.6\text{g}/\text{cm}^3$ である。厚み方向に $2.9\text{MPa}$ の様な面圧を加えたときの電極基材の密度は、電極基材の目付と厚み方向に $2.9\text{MPa}$ の様な面圧を加えたときの電極基材の厚みから計算によって求める。電極基材

は、拡散・透過性を高くするためには気孔率を高くする必要があるが、厚み方向に 2.9 MPa のような面圧を加えたときの密度が  $0.8 \text{ g/cm}^3$  よりも大きくなると気孔率が下がり、拡散・透過性が不十分になる。また、 $0.3 \text{ g/cm}^3$  よりも小さいと、厚み方向の抵抗値が大きくなる。

【0071】電極基材は、厚み方向への面圧による加圧を行わない状態で、厚み方向に  $14 \text{ cm/秒}$  の空気を透過させたときの圧力損失が、 $98 \text{ Pa}$  ( $10 \text{ mmAq}$ ) 以下であるのが電極基材のガス拡散性の点で好ましい。より好ましいのは  $29 \text{ Pa}$  ( $3 \text{ mmAq}$ ) 以下であり、さらに好ましいのは  $9.8 \text{ Pa}$  ( $1 \text{ mmAq}$ ) 以下である。

【0072】電極基材の引っ張り強さは、 $0.49 \text{ N/10 mm}$  幅以上が好ましく、 $1.96 \text{ N/10 mm}$  幅以上がより好ましく、 $4.9 \text{ N/10 mm}$  幅以上が更に好ましい。引っ張り強さが低いと、電極基材の高次加工において、シートが破損する可能性が増すという問題がある。

【0073】多孔質導電性シートの電気抵抗は、 $100 \text{ m}\Omega \cdot \text{cm}^2$  以下であることが好ましく、 $50 \text{ m}\Omega \cdot \text{cm}^2$  以下であることがより好ましく、 $15 \text{ m}\Omega \cdot \text{cm}^2$  以下であることが更に好ましい。後述のように撥水性のフッ素樹脂を含む電極基材の電気抵抗は、 $150 \text{ m}\Omega \cdot \text{cm}^2$  以下であることが好ましく、 $70 \text{ m}\Omega \cdot \text{cm}^2$  以下であることがより好ましく、 $30 \text{ m}\Omega \cdot \text{cm}^2$  以下であることが更に好ましい。

【0074】電極基材には、上記に加え、実質的に二次元平面内において無作為な方向に配向された無機導電性繊維を高分子物質で結着してなる紙状シートを含み、無機導電性繊維の長さが、少なくとも  $3 \text{ mm}$  で、かつ、シートの厚みの少なくとも  $5$  倍である多孔質導電シートを用いることもできる。ここで、シートの厚みは JIS P 8118 に準じて測定する。測定時の面圧は  $13 \text{ kPa}$  とする。無機導電性繊維が実質的に二次元平面内において配向されているということの意味は、無機導電性繊維がおおむね一つの面を形成するように横たわっているという意味である。このことにより無機導電性繊維による対極との短絡や無機導電性繊維の折損を防止することができる。

【0075】電極基材の強度やハンドリング性を高くし、無機導電性繊維を実質的に二次元平面内において配向させるために、無機導電性繊維の長さは少なくとも  $3 \text{ mm}$  以上が好ましく、より好ましくは  $4.5 \text{ mm}$  以上、さらに好ましくは  $6 \text{ mm}$  以上とする。 $3 \text{ mm}$  未満では、強度、ハンドリング性を保つのが難しくなる。ただし、繊維長の異なる無機導電性繊維を混合することも好ましいものであり、この場合は、長い繊維長の無機導電性繊維が  $3 \text{ mm}$  以上であることが好ましく、短い繊維長の無機導電性繊維は  $3 \text{ mm}$  未満であっても構わない。また、

無機導電性繊維を実質的に二次元平面内において無作為な方向に配向させるために、無機導電性繊維の長さは電極基材の厚みの  $5$  倍以上、好ましくは  $8$  倍以上、さらに好ましくは  $12$  倍以上とする。 $5$  倍未満では、二次元への配向の確保が難しくなる。無機導電性繊維の長さの上限は、実質的に二次元平面内において無作為な方向に配向させるためには  $30 \text{ mm}$  以下が好ましく、 $15 \text{ mm}$  以下がより好ましく、 $8 \text{ mm}$  以下がさらに好ましい。無機導電性繊維が長すぎると分散不良を発生しやすく、多数の繊維が束状のまま残る場合がある。その場合、束状の部分は空隙率が低く、加圧時の厚みが厚くなるために加圧時に高い圧力がかかり、電極基材の破壊や、高分子電解質膜や電極触媒層の局所的な薄層化等の問題が起こりやすくなる。

【0076】電極基材の作成において、無機導電性繊維を実質的に二次元平面内において無作為な方向に配向させる方法としては、液体の媒体中に無機導電性繊維を分散させて抄造する湿式法や、空気中で無機導電性繊維を分散させて降り積もらせる乾式法がある。無機導電性繊維を確実に実質的に二次元平面内において配向させるため、また、無機導電性繊維の強度を高くするためには、湿式法、特にいわゆる抄紙法が好ましい。

【0077】電極基材に用いられる無機導電性繊維が炭素繊維の場合は、ポリアクリロニトリル (PAN) 系炭素繊維、フェノール系炭素繊維、ピッチ系炭素繊維、レーヨン系炭素繊維などが例示される。なかでも、PAN 系炭素繊維が好ましい。PAN 系炭素繊維はピッチ系炭素繊維にくらべて圧縮強さ、引張破断強度が大きく、折れにくい。このことは、炭素繊維を構成する炭素の結晶化の相異によると考えられる。折れにくい炭素繊維を得るためには、炭素繊維の熱処理温度は  $2,500^\circ\text{C}$  以下が好ましく、 $2,000^\circ\text{C}$  以下がより好ましい。

【0078】本発明の電極基材中に用いられる炭素短繊維は、直径  $D$  ( $\mu\text{m}$ ) と、引張強さ  $\sigma$  (MPa) と、引張弾性率  $E$  (MPa) との関係が次式を満足しているのがよい。そのような炭素短繊維からなる電極基材は、壊れにくいためである。すなわち、炭素短繊維の直径が細く、引張強さが強く、引張弾性率が低いほうが炭素短繊維は折れにくく、加圧時に電極基材が壊れにくくなる。

$$\sigma / (E \times D) \geq 0.5 \times 10^{-3}$$

ここで、炭素繊維の引張強さ、引張弾性率は JIS R 7601 に準じて測定する。偏平な断面の炭素繊維の場合、長径 ( $a$ ) と短径 ( $b$ ) の平均値  $((a+b)/2)$  を直径とする。種類の異なる炭素短繊維が混合されている場合、 $D$ 、 $\sigma$ 、 $E$  についてそれぞれ重量平均した値を用いる。好ましくは  $\sigma / (E \times D) \geq 1.1 \times 10^{-3}$  であり、より好ましくは  $\sigma / (E \times D) \geq 2.4 \times 10^{-3}$  である。

【0079】炭素短繊維の引張破断伸度は、電極基材の強度のため、 $0.7\%$  以上であるのが好ましく、より好

ましくは1.2%以上であり、さらに好ましくは1.8%以上である。引張破断伸度は引張強さ( $\sigma$ )を引張弾性率(E)で除した値である。

【0080】電極基材に用いられる無機導電性繊維の直径は、 $20\mu\text{m}$ 以下であるのが好ましい。より好ましいのは $12\mu\text{m}$ 以下、さらに好ましいのは $8\mu\text{m}$ 以下である。電極基材の表面には、無機導電性繊維の直径の5~10倍の直径の空隙が観察される。この空隙は繊維径が太くなると大きくなる。

【0081】電極基材に用いられる無機導電性繊維の体積抵抗率は、電極基材の低抵抗化のため $200\mu\Omega\cdot\text{m}$ 以下が好ましく、 $50\mu\Omega\cdot\text{m}$ 以下がより好ましく、 $15\mu\Omega\cdot\text{m}$ 以下がさらに好ましい。無機導電性繊維の体積抵抗率の測定はJIS R7601に準じて行う。前記測定処方で定められた繊維長さが得られない場合、得られた繊維長さで測定を行う。

【0082】電極基材は、水の滞留によるガス拡散・透過性の低下を防ぐために行う撥水处理、水の排出路を形成するための部分的撥水、親水处理や、抵抗を下げるために行われる炭素質粉末の添加等を行うことも好ましい実施態様である。

【0083】電極基材は、上述のように導電性無機繊維からなる多孔質導電シートを用いる場合、圧縮時の厚み低下抑制、密度の向上、電気抵抗の低減などの点から、導電性粒子、特に導電性無機粒子を含むことも好ましい実施態様である。このような導電性無機粒子としては、電気抵抗や耐食性の点から炭素材、特に炭素粒子が好ましい。

【0084】特に、柔軟性を有する導電性無機粒子がシート状に配列されてなる多孔質導電シートを電極基材に用いることも好ましい。これにより構成成分の脱落が少ない、あるいは、機械的力が作用しても壊れ難く、電気抵抗が低く、かつ、安価な電極基材を提供するという目的が可能となる。特に、柔軟性を有する導電性無機粒子として、膨張黒鉛粒子を用いることで上記目的が達成可能である。

【0085】ここで、膨張黒鉛粒子とは、黒鉛粒子が、硫酸、硝酸などにより層間化合物化された後、急速に加熱することにより膨張せしめられて得られる黒鉛粒子をいう。通常、膨張黒鉛粒子の結晶構造における層間距離は、原料黒鉛粒子のその約50~500倍である。

【0086】膨張黒鉛粒子は、それ自体、形状の変形性に富む。この性質は、柔軟性と云う言葉で表現される。この柔軟性は、膨張黒鉛粒子とそれに隣接する他の物体に対する膨張黒鉛粒子の形態的融和性により観察される。この形態的融和性は、膨張黒鉛粒子同士が、少なくとも一部が重なり合った状態で加圧作用を受けると、加圧状態に応じて、互いに変形し、粒子同士が少なくとも部分的に接合することにより観察される。また、この形態的融和性は、膨張黒鉛粒子と、気体透過性が確保され

る状態でそれらがシート状に配列せしめられる場合に用いられる補助材(例えば、カーボンブラックなどの従来用いられている柔軟性を有しない導電性無機粒子、あるいは、炭素繊維などの従来用いられている無機導電性繊維)とが、共に加圧された場合、膨張黒鉛粒子が、補助材の外形状に沿って、変形され、この補助材に接合されることにより観察される。

【0087】本発明の電極基材は、柔軟性を有する導電性微粒子に加えて、他の導電性粒子や導電性繊維を含むことも好ましい実施態様であるが、この導電性繊維と導電性粒子の双方が、無機材料からなることにより、耐熱性、耐酸化性、耐溶出性に優れた電極基材が得られる。柔軟性を有しない導電性無機粒子としては、例えば、カーボンブラック粉末、黒鉛粉末、金属粉末、セラミックス粉末などを含んでも良いが、電子導性と耐熱性の点から、カーボンブラック、黒鉛質や炭素質の炭素材が好ましく挙げられる。このような炭素材としては、オイルファーネスブラック、チャンネルブラック、ランプブラック、サーマルブラック、アセチレンブラックなどのカーボンブラックが、電子導性と比表面積の大きさから好ましいものである。オイルファーネスブラックとしては、キャボット社製バルカンXC-72、バルカンP、ブラックパールズ880、ブラックパールズ1100、ブラックパールズ1300、ブラックパールズ2000、リーガル400、ライオン社製ケッチェンブラックEC、三菱化学社製#3150、#3250などが挙げられ、アセチレンブラックとしては電気化学工業社製デンカブラックなどが挙げられる。またカーボンブラックのほか、天然の黒鉛、ピッチ、コークス、ポリアクリロニトリル、フェノール樹脂、フラン樹脂などの有機化合物から得られる人工黒鉛や炭素などがある。また、これら炭素材を後処理加工した炭素材も用いることが可能である。このような炭素材の中でも、特に、キャボット社製のバルカンXC-72、電気化学工業社製のデンカブラック、ライオン社製のケッチェンブラックなどが電子導性の点から好ましく用いられる。

【0088】なお、電極基材に対する導電性粒子の添加量としては、要求される電極特性や用いられる物質の比表面積や電子抵抗などに応じて適宜決められるべきものであるが、電極基材中の重量比率として1~80%が好ましく、20~60%がさらに好ましい。電子伝導体は、少ない場合は電子抵抗が低くなり、多い場合はガス透過性を阻害するなど、いずれも電極性能を低下させる。

【0089】電極基材は、上記の導電性粒子のほか、高分子物質を添加することも可能である。これにより圧縮や引張りに強くなり、強度、ハンドリング性を高め、無機導電性物質が電極基材から外れたり、電極基材の厚み方向を向くのを防止できる。特に、無機導電性短繊維を抄紙して多孔質導電シートからなる電極基材を作成する

際には、高分子物質を結着剤として用いることは重要である。高分子物質を結着させる方法としては、無機導電性物質を実質的に二次元平面内において無作為な方向に配向させるときに繊維状、粒状、液状の高分子物質を混合する方法と、無機導電性物質が実質的に二次元平面内において無作為な方向に配向された集合体に繊維状、液状の高分子物質を付着させる方法等がある。液状の概念には、高分子物質が溶解している溶液と共に、溶媒中に高分子物質の微粒子が分散して実質的に液体として取り扱うことができるものも含まれる。

【0090】無機導電性物質を結着する高分子物質としては、炭素またはケイ素を主鎖に持つ高分子物質が好ましく、たとえば、ポリビニルアルコール（PVA）、ポリ酢酸ビニル（酢ビ）、ポリエチレンテレフタレート（PET）、ポリプロピレン（PP）、ポリエチレン、ポリスチレン、ポリ塩化ビニル、ポリ塩化ビニリデン、アクリル樹脂、ポリウレタン等の熱可塑性樹脂や、フェノール樹脂、エポキシ樹脂、メラミン樹脂、尿素樹脂、アルキド樹脂、不飽和ポリエステル樹脂、アクリル樹脂、ポリウレタン樹脂等の熱硬化性樹脂のほか、熱可塑性エラストマー、ブタジエン・スチレン共重合体（SBR）、ブタジエン・アクリロニトリル共重合体（NBR）等のエラストマー、ゴム、セルロース、パルプ等を用いることができる。フッ素樹脂等の撥水性の樹脂を用い、無機導電性物質の結着と同時に電極基材の撥水化処理を行ってもよい。

【0091】本発明の膜-電極複合体が固体高分子型燃料電池として用いられる場合、カソード（空気極、酸素極）において、電極反応生成物としての水や、電解質を浸透した水が発生する。また、アノード（燃料極）においては、高分子電解質膜の乾燥防止のために燃料を加湿して供給する。これらの水の結露と滞留、水による高分子物質の膨潤が電極反応物を供給する際の妨げになるので、電極基材に含まれる高分子物質の吸水率は低いほうがよい。好ましくは20%以下、より好ましくは7%以下である。

【0092】このような点から、電極基材には撥水性の高分子を含むことも好ましい実施態様である。特にポリテトラフルオロエチレン（PTFE）、テトラフルオロエチレン-ヘキサフルオロプロピレン共重合体（FEP）、テトラフルオロエチレン-パーフルオロアルキルビニルエーテル共重合体（PFA）などのフッ素原子を含有するポリマ（フッ素樹脂）が高い撥水性を有するため好ましく用いられる。

【0093】上記のような高分子物質の電極基材に対する含有率は、0.1~50重量%の範囲にあるのが好ましい。電極基材の電気抵抗を低くするためには、高分子物質の含有率は少ないほうがよいが、0.1重量%未満ではハンドリングに耐える強度が不足し、無機導電性物質の脱落も多くなる。逆に、50重量%を超えると電極

基材の電気抵抗が増えてくるという問題が生じる。より好ましくは、10~30重量%の範囲である。

【0094】電極基材に添加した高分子物質は、200℃以上で焼成することも好ましい実施態様である。撥水処理に用いられる上記のフッ素樹脂は、融点以上に加熱することで、撥水性と結着性が向上する。また、フッ素樹脂以外の高分子物質においても、焼成により結着力が向上するほか、電気抵抗の低下、耐食性の向上が見られる。特にフッ素樹脂以外の高分子物質においては、耐酸化性に乏しい場合があり、燃料電池などの電気化学装置用電極として用いる際には、使用中に電極性能の低下をもたらす可能性がある。このため、電極作成時には結着剤として高分子物質を用い、電極として使用する前に焼成して炭化乃至は分解除去等の処理をしておくことが好ましい。

【0095】本発明の膜-電極複合体の製造方法としては、特に限定されるものではない。一般的には、電極基材、電極触媒層、プロトン交換膜、電極触媒層、電極基材の順で積層して接合するが、この接合条件についても電極触媒層あるいは電気化学装置の特性に応じて適宜決められるべきものである。接合方法としては、加温プレスが好ましい方法であり、この条件についても特に限定されるものではないが、プレス温度は20℃~200℃、プレス圧力は1MPa~20MPaである。

【0096】本発明の電極触媒層と電極基材とからなる電極、あるいは該電極とプロトン交換膜からなる膜-電極複合体（MEA）は、種々の電気化学装置に適応することができる。なかでも燃料電池や水電解層が好ましく、さらに燃料電池のなかでも固体高分子型燃料電池に好適である。燃料電池には、水素を燃料とするものとメタノールなどの炭化水素を燃料とするものがあるが、特に限定されることなく用いることができる。

【0097】さらに、本発明の電極触媒層を用いた燃料電池の用途としては、特に限定されることなく考えられるが、固体高分子型燃料電池において有用な用途である移動体の電力供給源が好ましいものである。特に、乗用車、バス、トラックなどの自動車や船舶、鉄道なども好ましい移動体である。

【0098】

【実施例】以下本発明の詳細につき実施例を用いてさらに説明する。

【0099】実施例1

（1）多孔質導電シートを作成

PAN系炭素繊維（東レ製トレカT-300）を3mmに裁断した。この短繊維炭素繊維をポリビニルアルコール繊維とともに水に分散させた。この分散液を金網上に抄紙することにより炭素繊維抄紙体を作成した。

【0100】次にこの抄紙体をPFAディスパージョン（ダイキン工業社製ネオフロンPFAディスパージョン）に含浸し、乾燥した。さらに、370℃で3時間熱



処理を行い、PFAが3重量%付着したPAN系炭素短繊維からなる多孔質導電シートを作成した。この多孔質導電シートの目付は3g/m<sup>2</sup>、厚さは20μmであった。

#### 【0101】(2) 触媒-ポリマ複合体の作成

市販のAldrich社製Nafion溶液(5重量%) 5gに触媒担持カーボン(触媒; Pt、カーボン; Cabot社製VulcanXC-72、白金担持量; 30wt%) 2gとi-プロパノールを加え、良く攪拌して触媒-ポリマ複合体を含む分散液を調製した。

#### 【0102】(3) 触媒層の作成

前記(1)で作成した多孔質導電シートを前記(2)で作成した触媒-ポリマ複合体を含む分散液に含浸後、乾燥させて、多孔質導電シートと触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み30μm、白金の付き量; 0.5mg/cm<sup>2</sup>、Nafionの付き量; 0.2mg/cm<sup>2</sup>であった。

#### 【0103】(4) 膜-電極複合体(MEA)の作成

前記(3)で作成した触媒層2枚と、電極基材として撥水処理を行った炭素繊維紡績糸織物(E-TEK社製ELAT、PFAの付き量20%) 2枚、プロトン交換膜としてDuPont社製Nafion112を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス(温度120℃、圧力50MPa)を行うことで膜-電極複合体を作成した。

#### 【0104】(5) 燃料電池評価

前記(4)で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度; 60℃、燃料ガス; 水素、酸化ガス; 空気、ガス利用率; アノード70%/カソード40%において電流-電圧(I-V)測定を行ったところ、最高出力は、600mW/cm<sup>2</sup>であった。

#### 【0105】比較例1

##### (1) 触媒層の塗工

実施例1(2)において、i-プロパノールを加えずに作成した触媒-ポリマ複合体を含んだ分散液を、実施例1で使用した電極基材上にスクリーン塗工、乾燥することにより触媒層(厚み40μm、白金の付き量; 0.5mg/cm<sup>2</sup>、Nafionの付き量; 0.2mg/cm<sup>2</sup>)つき電極基材を作成した。

#### 【0106】(2) 膜-電極複合体の作成および評価

前記(1)で作成した触媒層つき電極基材2枚と実施例1で使用したプロトン交換膜を用意した。触媒層をプロトン交換膜に対向させて、触媒層付き電極基材/プロトン交換膜/触媒層付き電極基材をこの順で積層し、実施例1と同様に熱プレスを行うことで膜-電極複合体を作成した。

【0107】この膜-電極複合体を実施例1と同条件にて固体高分子型燃料電池セルを作成および評価した。最

高出力は200mW/cm<sup>2</sup>であり、実施例1に比べて悪い性能であった。特に活性化分極による電圧低下が大きく、これは触媒塗液の電極基材への浸み込みが原因と考えられる。

#### 【0108】実施例2

##### (1) 多孔質導電シートの作成

PAN系炭素繊維(東レ製トレカT-300)を12mmと1mmに裁断した。この12mmに裁断した短繊維炭素繊維をポリビニルアルコール繊維とともに水に分散させた。この分散液を金網上に抄紙することにより炭素繊維抄紙体を作成した。

【0109】次に、この抄紙体を1mmに裁断した短繊維炭素繊維を分散したPFAディスパージョン(ダイキン工業社製ネオフロンPFAディスパージョン)に含浸し、乾燥した。さらに、370℃で3時間熱処理を行い、PFAが3重量%付着したPAN系炭素短繊維(12mmと1mmの重量比60:40)からなる多孔質導電シートを作成した。この多孔質導電シートの目付は3g/m<sup>2</sup>、厚さは15μmであった。

#### 【0110】(2) 触媒-ポリマ複合体の作成

市販のAldrich社製Nafion溶液(5重量%) 5gに触媒担持カーボン(触媒; Pt、カーボン; Cabot社製VulcanXC-72、白金担持量; 50wt%) 1.25gとi-プロパノールを加え、良く攪拌して触媒-ポリマ複合体を含む分散液を調製した。

#### 【0111】(3) 触媒層の作成

前記(1)で作成した多孔質導電シートを前記(2)で作成した触媒-ポリマ複合体を含む分散液に含浸後、乾燥させて、多孔質導電シートと触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み20μm、白金の付き量; 0.5mg/cm<sup>2</sup>、Nafionの付き量; 0.2mg/cm<sup>2</sup>であった。

#### 【0112】(4) 膜-電極複合体(MEA)の作成

前記(3)で作成した触媒層2枚と、電極基材として撥水処理を行った炭素繊維紡績糸織物(E-TEK社製ELAT、PFAの付き量25%) 2枚、プロトン交換膜としてDuPont社製Nafion112を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス(温度120℃、圧力50MPa)を行うことで膜-電極複合体を作成した。

#### 【0113】(5) 燃料電池評価

前記(4)で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度; 60℃、燃料ガス; 水素、酸化ガス; 空気、ガス利用率; アノード70%/カソード40%において電流-電圧(I-V)測定を行ったところ、最高出力は、650mW/cm<sup>2</sup>であった。

#### 【0114】比較例2

##### (1) 多孔質導電シートの作成

PAN系炭素繊維（東レ製トレカT-300）を12mmと1mmに裁断した。この12mmに裁断した短繊維炭素繊維をポリビニルアルコール繊維とともに水に分散させた。この分散液を金網上に抄紙することにより炭素繊維抄紙体を作成した。

【0115】次に、この抄紙体を1mmに裁断した短繊維炭素繊維を分散したPFAディスパージョン（ダイキン工業社製ネオフロンPFAディスパージョン）に含浸し、乾燥した。さらに、370℃で3時間熱処理を行い、PFAが3重量%付着したPAN系炭素短繊維（12mmと1mmの重量比60:40）からなる多孔質導電シートを作成した。この多孔質導電シートの目付は20g/m<sup>2</sup>、厚さは80μmであった。

【0116】（2）触媒-ポリマ複合体の作成  
市販のAldrich社製Nafion溶液（5重量%）5gに触媒担持カーボン（触媒；Pt、カーボン；Cabot社製VulcanXC-72、白金担持量；50wt%）1.25gとi-プロパノールを加え、良く攪拌して触媒-ポリマ複合体を含む分散液を調製した。

【0117】（3）触媒層の作成  
前記（1）で作成した多孔質導電シートを前記（2）で作成した触媒-ポリマ複合体を含む分散液に含浸後、乾燥させて、多孔質導電シートと触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み80μm、白金の付着量；0.5mg/cm<sup>2</sup>、Nafionの付着量；0.2mg/cm<sup>2</sup>であった。

【0118】（4）膜-電極複合体（MEA）の作成  
前記（3）で作成した触媒層2枚を用い、実施例2と同様に膜-電極複合体を作成した。

【0119】（5）燃料電池評価  
前記（4）で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成し、実施例2と同条件で電流-電圧（I-V）測定を行ったところ、最高出力は、350mW/cm<sup>2</sup>であり、活性化分極と拡散分極が大きく性能は不良であった。

#### 【0120】実施例3

##### （1）多孔質導電シートの作成

PAN系炭素繊維（東レ製トレカT-300）を6mmに裁断した。この6mmに裁断した短繊維炭素繊維をポリビニルアルコール繊維とともに水に分散させた。この分散液を金網上に抄紙することにより炭素繊維抄紙体を作成した。

【0121】次に、この抄紙体をカーボンブラックとしてアセチレンブラック（電気化学工業社製デンカブラック）を分散したPFAディスパージョン（ダイキン工業社製ネオフロンPFAディスパージョン）に含浸し、乾燥した。さらに、370℃で3時間熱処理を行い、アセチレンブラックが5重量%、PFAが10重量%付着したPAN系炭素短繊維からなる多孔質導電シートを作成

した。この多孔質導電シートの目付は3g/m<sup>2</sup>、厚さは13μmであった。

【0122】（2）触媒-ポリマ複合体の作成  
市販のAldrich社製Nafion溶液（5重量%）5gに触媒担持カーボン（触媒；Pt、カーボン；Cabot社製VulcanXC-72、白金担持量；40wt%）0.78gとエタノールを加え、良く攪拌して触媒-ポリマ複合体を含む分散液を調製した。

##### 【0123】（3）触媒層の作成

前記（1）で作成した多孔質導電シートを前記（2）で作成した触媒-ポリマ複合体を含む分散液に含浸後、乾燥させて、多孔質導電シートと触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み15μm、白金の付着量；0.4mg/cm<sup>2</sup>、Nafionの付着量；0.32mg/cm<sup>2</sup>であった。

【0124】（4）膜-電極複合体（MEA）の作成  
前記（3）で作成した触媒層2枚と、電極基材として撥水処理を行った炭素繊維紡績糸織物（E-TEK社製ELAT、PFAの付着量25%）2枚、プロトン交換膜としてDuPont社製Nafion112を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス（温度120℃、圧力40MPa）を行うことで膜-電極複合体を作成した。

##### 【0125】（5）燃料電池評価

前記（4）で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度；80℃、燃料ガス；水素、酸化ガス；空気、ガス利用率；アノード70%/カソード40%において電流-電圧（I-V）測定を行ったところ、最高出力は、70.0mW/cm<sup>2</sup>であった。

#### 【0126】比較例3

##### （1）触媒層の塗工

実施例3（2）において、エタノールを加えずに作成した触媒-ポリマ複合体を含んだ分散液を、実施例3で使用した炭素繊維紡績糸織物電極上にカーボンブラックを塗工した電極基材（アセチレンブラックが80重量%、PFAが20重量%を10mg/cm<sup>2</sup>付着した）上にスクリーン塗工、乾燥することにより触媒層（厚み15μm、白金の付着量；0.4mg/cm<sup>2</sup>、Nafionの付着量；0.32mg/cm<sup>2</sup>）つき電極基材を作成した。

【0127】（2）膜-電極複合体の作成および評価  
前記（1）で作成した触媒層つき電極基材2枚と実施例1で使用したプロトン交換膜を用意した。触媒層をプロトン交換膜に対向させて、触媒層付き電極基材/プロトン交換膜/触媒層付き電極基材をこの順で積層し、実施例3と同様に熱プレスを行うことで膜-電極複合体を作成した。

【0128】この膜-電極複合体を実施例3と同条件に

て固体高分子型燃料電池セルを作成および評価した。最高出力は  $400 \text{ mW/cm}^2$  であり、実施例 3 に比べて悪い性能であった。特にガス拡散性の低下に伴う活性化分極による電圧低下が大きく、これは炭素繊維紡績糸織物電極上にカーボンブラックを塗工したことが原因と考えられる。

#### 【0129】実施例 4

##### (1) 多孔質導電シートの作成

PAN 系炭素繊維（東レ製トレカ T-300）を  $3 \text{ mm}$  と  $0.1 \text{ mm}$  に裁断した。この  $3 \text{ mm}$  に裁断した短繊維炭素繊維をポリビニルアルコール繊維とともに水に分散させた。この分散液を金網上に抄紙することにより炭素繊維抄紙体を作成した。

【0130】次に、この抄紙体を  $0.1 \text{ mm}$  に裁断した短繊維炭素繊維を分散した PFA ディスパーション（ダイキン工業社製ネオフロン PFA ディスパーション）に含浸し、乾燥した。さらに、 $370^\circ\text{C}$  で 3 時間熱処理を行い、PFA が 3 重量% 付着した PAN 系炭素短繊維（ $3 \text{ mm}$  と  $0.1 \text{ mm}$  の重量比 80:20）からなる多孔質導電シートを作成した。この多孔質導電シートの目付は  $5 \text{ g/m}^2$ 、厚さは  $15 \mu\text{m}$  であった。

【0131】(2) 触媒-ポリマ複合体の作成  
市販の Aldrich 社製 Nafion 溶液（5 重量%） $5 \text{ g}$  に触媒担持カーボン（触媒；Pt、カーボン；Cabot 社製 Vulcan XC-72、白金担持量；50 wt%） $0.63 \text{ g}$  を良く攪拌して触媒-ポリマ複合体を含む分散液を調製した。

【0132】(3) 触媒層の作成  
前記 (1) で作成した多孔質導電シート上に前記 (2) で作成した触媒-ポリマ複合体を含む分散液をスクリーン印刷にて塗工後、乾燥させて、多孔質導電シートと触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み  $20 \mu\text{m}$ 、白金の付き量； $0.4 \text{ mg/cm}^2$ 、Nafion の付き量； $0.32 \text{ mg/cm}^2$  であった。

【0133】(4) 電極基材の作成  
長さ  $12 \text{ mm}$  にカットされた PAN 系炭素繊維の短繊維と膨張黒鉛粉末（東洋炭素（株）製、かさ密度  $0.14 \text{ g/cm}^3$ 、平均粒径  $100$  乃至  $200 \mu\text{m}$ ）を、重量比で 1:1 に混合し、ナトリウムカルボキシメチルセルローズ水溶液中に分散した。この分散液を用い、炭素繊維の短繊維に膨張黒鉛粉末が付着したシートを金網上に抄造した。水分を除去する目的で、シートを 2 枚の濾紙に挟み軽く加圧した。その後、濾紙を外してシートを乾燥した。乾燥後、シートをロールプレスし、多孔質導電シートを製造した。得られたシートは  $80 \text{ g/m}^2$  であった。この多孔質導電シートを空气中で  $200^\circ\text{C}$ 、30 分の熱処理を行った後、PFA ディスパーション（ネオフロン PFA ディスパーション、ダイキン工業株式会社製）を含浸し、2 枚の濾紙に挟んで軽く加圧、乾燥した。さらにこのシートを、 $14.7 \text{ kPa}$  ( $0.15 \text{ k}$

$\text{gf/cm}^2$ ) で加圧しながら  $400^\circ\text{C}$ 、3 時間の熱処理を行い、電極基材を製造した。膨張黒鉛の付き量は 50 重量%、PFA の付き量は 15 重量% であった。

【0134】(5) 膜-電極複合体 (MEA) の作成  
前記 (3) で作成した触媒層 2 枚、前記 (4) で作成した電極基材 2 枚、プロトン交換膜として Du Pont 社製 Nafion 112 を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス（温度  $130^\circ\text{C}$ 、圧力  $50 \text{ MPa}$ ）を行うことで膜-電極複合体を作成した。

##### 【0135】(6) 燃料電池評価

前記 (5) で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度； $70^\circ\text{C}$ 、燃料ガス；水素、酸化ガス；空気、ガス利用率；アノード 70%/カソード 40% において電流-電圧 (I-V) 測定を行ったところ、最高出力は、 $500 \text{ mW/cm}^2$  であった。

#### 【0136】比較例 4

##### (1) 触媒層の塗工

実施例 4 (2) において作成した触媒-ポリマ複合体を含んだ分散液を、実施例 4 (4) で作成した多孔質導電シート上にカーボンブラックを塗工した電極基材上にスクリーン塗工、乾燥することにより触媒層（厚み  $20 \mu\text{m}$ 、白金の付き量； $0.4 \text{ mg/cm}^2$ 、Nafion の付き量； $0.32 \text{ mg/cm}^2$ ）つき電極基材を作成した。

【0137】(2) 膜-電極複合体の作成および評価  
前記 (1) で作成した触媒層つき電極基材 2 枚と実施例 1 で使用したプロトン交換膜を用意した。触媒層をプロトン交換膜に対向させて、触媒層付き電極基材/プロトン交換膜/触媒層付き電極基材をこの順で積層し、実施例 4 と同様に熱プレスを行うことで膜-電極複合体を作成した。

【0138】この膜-電極複合体を実施例 4 と同条件にて固体高分子型燃料電池セルを作成および評価した。最高出力は  $350 \text{ mW/cm}^2$  であり、実施例 4 に比べて悪い性能であった。特にガス拡散性の低下に伴う活性化分極による電圧低下が大きく、これは炭素繊維紡績糸織物電極上にカーボンブラックを塗工したことが原因と考えられる。

#### 【0139】実施例 5

##### (1) 多孔質導電シートの作成

PAN 系耐炭化系を短繊維にカットしてカード化した後、ウォータージェットパンチング法にて不織布加工し、 $1600^\circ\text{C}$  にて炭化処理を行った。この炭素繊維不織布をカーボンブラック（アセチレンブラック；電気化学工業社製デンカブラック）を分散した PTFE ディスパーション（ダイキン工業社製ポリフロン TFE ディスパーション）に含浸し、乾燥した。さらに、 $400^\circ\text{C}$  で 3 時間熱処理を行い、カーボンブラックが 10 重量%、

PTFEが20重量%付着したPAN系炭素短繊維不織布からなる多孔質導電シートを作成した。この多孔質導電シートの目付は $3\text{ g/m}^2$ 、厚さは $10\text{ }\mu\text{m}$ であった。

#### 【0140】(2) 触媒-ポリマ複合体の作成

市販のAldrich社製Nafion溶液(5重量%) 5gに触媒担持カーボン(触媒; Pt、カーボン; Cabot社製VulcanXC-72、白金担持量; 50wt%) 0.83gを加えて良く攪拌して触媒-ポリマ複合体を含む分散液を調製した。

#### 【0141】(3) 触媒層の作成

前記(1)で作成した多孔質導電シート上に前記(2)で作成した触媒-ポリマ複合体を含む分散液をスクリーン印刷にて塗工後、乾燥させて、多孔質導電シートと触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み $15\text{ }\mu\text{m}$ 、白金の付き量;  $0.4\text{ mg/cm}^2$ 、Nafionの付き量;  $0.24\text{ mg/cm}^2$ であった。

【0142】(4) 膜-電極複合体(MEA)の作成  
前記(3)で作成した触媒層2枚と、電極基材として撥水処理を行った炭素繊維ペーパー(東レ製TGP-H-060)2枚、プロトン交換膜としてDu Pont社製Nafion112を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス(温度 $150^\circ\text{C}$ 、圧力 $50\text{ MPa}$ )を行うことで膜-電極複合体を作成した。

#### 【0143】(5) 燃料電池評価

前記(4)で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度;  $80^\circ\text{C}$ 、燃料ガス; 水素、酸化ガス; 空気、ガス利用率; アノード70%/カソード40%において電流-電圧(I-V)測定を行ったところ、最高出力は、 $600\text{ mW/cm}^2$ であった。

#### 【0144】実施例6

##### (1) 多孔質導電シートの作成

PAN系耐炎化糸を短繊維にカットしてカード化した後、ウォータージェットパンチング法にて不織布加工し、 $1600^\circ\text{C}$ にて炭化処理を行い、多孔質導電シートを作成した。この多孔質導電シートの目付は $3\text{ g/m}^2$ 、厚さは $10\text{ }\mu\text{m}$ であった。

#### 【0145】(2) 触媒-ポリマ複合体の作成

PTFEディスパージョン(ダイキン工業社製ポリフロンTFEディスパージョン)に触媒担持カーボン(触媒; Pt、カーボン; Cabot社製VulcanXC-72、白金担持量; 50wt%)を加えてよく攪拌して触媒-ポリマ複合体を含む分散液を調製した。

#### 【0146】(3) 触媒層の作成

前記(1)で作成した多孔質導電シート上に前記(2)で作成した触媒-ポリマ複合体を含む分散液に含浸後、乾燥させて、多孔質導電シートと触媒-ポリマ複合体が

一体構造となった、自立可能なシートの触媒層を作成した。この触媒層を市販のAldrich社製Nafion溶液(5重量%)に含浸、乾燥してプロトン交換ポリマを含む触媒層を作成した。この触媒層は厚み $15\text{ }\mu\text{m}$ 、白金の付き量;  $0.4\text{ mg/cm}^2$ 、Nafionの付き量;  $0.2\text{ mg/cm}^2$ 、PTFEの付き量;  $0.2\text{ mg/cm}^2$ であった。

【0147】(4) 膜-電極複合体(MEA)の作成  
前記(3)で作成した触媒層2枚と、電極基材として撥水処理を行った炭素繊維紡績系織物(E-TEK社製ELAT)2枚、プロトン交換膜としてDu Pont社製Nafion112を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス(温度 $140^\circ\text{C}$ 、圧力 $50\text{ MPa}$ )を行うことで膜-電極複合体を作成した。

#### 【0148】(5) 燃料電池評価

前記(4)で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度;  $70^\circ\text{C}$ 、燃料ガス; 水素、酸化ガス; 空気、ガス利用率; アノード70%/カソード40%において電流-電圧(I-V)測定を行ったところ、最高出力は、 $600\text{ mW/cm}^2$ であった。

#### 【0149】実施例7

##### (1) 多孔質導電シートの作成

ポリフェニレンスルフィド繊維を短繊維にカットしてカード化した後、ニードルパンチング法にて不織布加工して非導電性不織布を作成した。この非導電性布帛をカーボンブラック(アセチレンブラック; 電機化学工業社製デンカブラック)を分散したPVDFのN-メチルピロリドン溶液に含浸し、直ちにメタノールに浸漬することにより湿式凝固を行った。これを乾燥し、PVDFが3重量%付着した多孔質導電シートを作成した。この多孔質導電シートの目付は $4\text{ g/m}^2$ 、厚さは $20\text{ }\mu\text{m}$ であった。

#### 【0150】(2) 触媒-ポリマ複合体の作成

市販のAldrich社製Nafion溶液(5重量%) 5gに触媒担持カーボン(触媒; Pt、カーボン; Cabot社製Black Pearls、白金担持量; 30wt%) 1.0gを加えて良く攪拌して触媒-ポリマ複合体を含む分散液を調製した。

#### 【0151】(3) 触媒層の作成

前記(1)で作成した多孔質導電シートを前記(2)で作成した触媒-ポリマ複合体を含む分散液に含浸後、乾燥させて、多孔質導電シートと触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み $25\text{ }\mu\text{m}$ 、白金の付き量;  $0.4\text{ mg/cm}^2$ 、Nafionの付き量;  $0.32\text{ mg/cm}^2$ であった。

#### 【0152】(4) 膜-電極複合体(MEA)の作成

前記(3)で作成した触媒層2枚と、電極基材として撥

水処理を行った炭素繊維ペーパー（東レ製TGP-H-060）2枚、プロトン交換膜としてDu Pont社製Nafion112を用意した。電極基材／触媒層／プロトン交換膜／触媒層／電極基材をこの順で積層し、熱プレス（温度130℃、圧力50MPa）を行うことで膜－電極複合体を作成した。

#### 【0153】（5）燃料電池評価

前記（4）で作成した膜－電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度；70℃、燃料ガス；水素、酸化ガス；空気、ガス利用率；アノード70％／カソード40％において電流－電圧（I－V）測定を行ったところ、最高出力は、600mW/cm<sup>2</sup>であった。

#### 【0154】実施例8

##### （1）多孔質導電シートの作成

PAN系耐酸化系を短繊維にカットしてカード化した後、ニードルパンチング法にて不織布加工し、1400℃にて炭化処理を行い、多孔質導電シートを作成した。この多孔質導電シートの目付は3g/m<sup>2</sup>、厚さは15μmであった。

##### 【0155】（2）触媒－ポリマ複合体の作成

市販のAldrich社製Nafion溶液（5重量％）を濃縮し、15重量％とした。この溶液5gに触媒担持カーボン（触媒；Pt、カーボン；Cabot社製VulcanXC-72、白金担持量；50wt％）1.88gを加えて良く攪拌して触媒－ポリマ複合体を含む分散液を調製した。

##### 【0156】（3）触媒層の作成

前記（1）で作成した多孔質導電シートを前記（2）で作成した触媒－ポリマ複合体を含む分散液に含浸後、直ちにメタノールに含浸して湿式凝固を行い、乾燥させ、多孔質導電シートと触媒－ポリマ複合体が一体構造となり微多孔質構造を有する自立可能なシートの触媒層を作成した。この触媒層は厚み25μm、白金の付き量；0.3mg/cm<sup>2</sup>、Nafionの付き量；0.24mg/cm<sup>2</sup>であった。

【0157】（4）膜－電極複合体（MEA）の作成  
前記（3）で作成した触媒層2枚と、電極基材として撥水処理を行った炭素繊維ペーパー（東レ製TGP-H-060）2枚、プロトン交換膜としてDu Pont社製Nafion112を用意した。電極基材／触媒層／プロトン交換膜／触媒層／電極基材をこの順で積層し、熱プレス（温度150℃、圧力50MPa）を行うことで膜－電極複合体を作成した。

##### 【0158】（5）燃料電池評価

前記（4）で作成した膜－電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度；80℃、燃料ガス；水素、酸化ガス；空気、ガス利用率；アノード70％／カソード40％において電流－電圧（I－V）測定を行ったところ、最高出力は、700mW/cm<sup>2</sup>であった。

#### 【0159】実施例9

##### （1）非導電性布帛の作成

PTFE繊維（東レ製トヨフロン）を3mmに裁断した。この裁断した短繊維PTFEをカルボキシメチルセルロース（CMC）水溶液に分散させた。この分散液を金網上に抄紙することによりPTFE抄紙体を作成した。

【0160】次に、この抄紙体を370℃で3時間加圧熱処理を行い、非導電性布帛を作成した。この非導電性布帛の目付は10g/m<sup>2</sup>、厚さは20μmであった。

##### 【0161】（2）触媒－ポリマ複合体の作成

市販のAldrich社製Nafion溶液（5重量％）5gに触媒担持カーボン（触媒；Pt、カーボン；Cabot社製VulcanXC-72、白金担持量；50wt％）1.25gとi-プロパノールを加え、良く攪拌して触媒－ポリマ複合体を含む分散液を調製した。

##### 【0162】（3）触媒層の作成

前記（1）で作成した非導電性布帛を前記（2）で作成した触媒－ポリマ複合体を含む分散液に含浸後、乾燥させて、非導電性布帛と触媒－ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み20μm、白金の付き量；0.5mg/cm<sup>2</sup>、Nafionの付き量；0.2mg/cm<sup>2</sup>であった。

##### 【0163】（4）膜－電極複合体（MEA）の作成

前記（3）で作成した触媒層2枚と、電極基材として撥水処理を行った炭素繊維紡績糸織物（E-TEK社製ELAT、PFAの付き量25％）2枚、プロトン交換膜としてDu Pont社製Nafion112を用意した。電極基材／触媒層／プロトン交換膜／触媒層／電極基材をこの順で積層し、熱プレス（温度130℃、圧力50MPa）を行うことで膜－電極複合体を作成した。

##### 【0164】（5）燃料電池評価

前記（4）で作成した膜－電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度；60℃、燃料ガス；水素、酸化ガス；空気、ガス利用率；アノード70％／カソード40％において電流－電圧（I－V）測定を行ったところ、最高出力は、650mW/cm<sup>2</sup>であった。

#### 【0165】比較例5

##### （1）触媒層の塗工

実施例9（2）において、i-プロパノールを加えずに作成した触媒－ポリマ複合体を含んだ分散液を、実施例9で使用した電極基材上にスクリーン塗工、乾燥することにより触媒層（厚み30μm、白金の付き量；0.5mg/cm<sup>2</sup>、Nafionの付き量；0.2mg/cm<sup>2</sup>）付き電極基材を作成した。

##### 【0166】（2）膜－電極複合体の作成および評価

前記（1）で作成した触媒層付き電極基材2枚と実施例9で使用したプロトン交換膜を用意した。触媒層をプロ

トン交換膜に対向させて、触媒層付き電極基材／プロトン交換膜／触媒層付き電極基材をこの順で積層し、実施例9と同様に熱プレス（温度130℃、圧力50MPa）を行うことで膜－電極複合体を作成した。

【0167】この膜－電極複合体を実施例1. 1と同条件にて固体高分子型燃料電池セルを作成および評価した。最高出力は200mW/cm<sup>2</sup>であり、実施例9に比べて悪い性能であった。特に活性化分極による電圧低下が大きく、これは触媒塗液の電極基材への浸み込みが原因と考えられる実施例10

#### (1) 非導電性布帛の作成

PFA繊維（東レ製トヨフロン）を3mmに裁断した。この裁断した短繊維PFAをCMC水溶液に分散させた。この分散液を金網上に抄紙することによりPFA抄紙体を作成した。

【0168】次に、この抄紙体を280℃で3時間熱処理を行うことにより非導電性布帛を作成した。この非導電性布帛を延伸することで目付は10g/m<sup>2</sup>、厚さは15μmがえられた。

#### 【0169】(2) 触媒－ポリマ複合体の作成

市販のAldrich社製Nafion溶液（5重量%）5gに触媒担持カーボン（触媒；Pt、カーボン；Cabot社製VulcanXC-72、白金担持量；50wt%）1.25gとエタノールを加え、良く攪拌して触媒－ポリマ複合体を含む分散液を調製した。

#### 【0170】(3) 触媒層の作成

前記(1)で作成した非導電性布帛を前記(2)で作成した触媒－ポリマ複合体を含む分散液に含浸後、乾燥させて、非導電性布帛と触媒－ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み15μm、白金の付き量；0.4mg/cm<sup>2</sup>、Nafionの付き量；0.16mg/cm<sup>2</sup>であった。

【0171】(4) 膜－電極複合体（MEA）の作成  
前記(3)で作成した触媒層2枚と、電極基材として撥水処理を行った炭素繊維紡績糸織物（E-TEK社製ELAT、PFAの付き量25%）2枚、プロトン交換膜としてDuPont社製Nafion112を用意した。電極基材／触媒層／プロトン交換膜／触媒層／電極基材をこの順で積層し、熱プレス（温度130℃、圧力50MPa）を行うことで膜－電極複合体を作成した。

#### 【0172】(5) 燃料電池評価

前記(4)で作成した膜－電極複合体をセバレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度；60℃、燃料ガス；水素、酸化ガス；空気、ガス利用率；アノード70%/カソード40%において電流－電圧（I-V）測定を行ったところ、最高出力は、650mW/cm<sup>2</sup>であった。

#### 【0173】比較例6

##### (1) 多孔質導電シートの作成

FEP繊維（東レ製トヨフロン）を3mmに裁断した。この3mmに裁断した短繊維PFAをポリビニルアルコール繊維とともに水に分散させた。この分散液を金網上に抄紙することによりPFA繊維抄紙体を作成した。

【0174】次に、この抄紙体を、250℃で3時間熱処理を行い、非導電性布帛を作成した。この多孔質導電シートの目付は40g/m<sup>2</sup>、厚さは80μmであった。

#### 【0175】(2) 触媒－ポリマ複合体の作成

市販のAldrich社製Nafion溶液（5重量%）5gに触媒担持カーボン（触媒；Pt、カーボン；Cabot社製VulcanXC-72、白金担持量；50wt%）1.25gとエタノールを加え、良く攪拌して触媒－ポリマ複合体を含む分散液を調製した。

#### 【0176】(3) 触媒層の作成

前記(1)で作成した非導電性布帛を前記(2)で作成した触媒－ポリマ複合体を含む分散液に含浸後、乾燥させて、非導電性布帛と触媒－ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み80μm、白金の付き量；0.4mg/cm<sup>2</sup>、Nafionの付き量；0.16mg/cm<sup>2</sup>であった。

【0177】(4) 膜－電極複合体（MEA）の作成  
前記(3)で作成した触媒層2枚を用い、実施例10と同様に膜－電極複合体を作成した。

#### 【0178】(5) 燃料電池評価

前記(4)で作成した膜－電極複合体をセバレータに挟み固体高分子型燃料電池セルを作成し、実施例10と同条件で電流－電圧（I-V）測定を行ったところ、最高出力は、350mW/cm<sup>2</sup>であり、活性化分極が大きく性能は不良であった。

#### 【0179】実施例11

##### (1) 非導電性布帛の作成

PTFE繊維（東レ製トヨフロン）を6mmに裁断した。この6mmに裁断した短繊維PFAをCMC水溶液に分散させた。この分散液を金網上に抄紙することによりPFA繊維抄紙体を作成した。

【0180】次に、この抄紙体をカーボンブラックとしてアセチレンブラック（電気化学工業社製デンカブラック）を分散したPFAディスパージョン（ダイキン工業社製ネオフロンPFAディスパージョン）に含浸し、乾燥した。さらに、370℃で3時間熱処理を行い、カーボンブラックの付き量が10重量%のPTFE短繊維からなる布帛を作成した。この布帛を延伸することで目付は3g/m<sup>2</sup>、厚さは13μmの非導電性布帛を得た。

#### 【0181】(2) 触媒－ポリマ複合体の作成

市販のAldrich社製Nafion溶液（5重量%）5gに触媒担持カーボン（触媒；Pt、カーボン；Cabot社製VulcanXC-72、白金担持量；40wt%）0.78gとエタノールを加え、良く攪拌して触媒－ポリマ複合体を含む分

散液を調製した。

#### 【0182】(3) 触媒層の作成

前記(1)で作成した布帛を前記(2)で作成した触媒-ポリマ複合体を含む分散液に含浸後、乾燥させて、布帛シートと触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み  $15\mu\text{m}$ 、白金の付き量； $0.4\text{mg}/\text{cm}^2$ 、Nafionの付き量； $0.32\text{mg}/\text{cm}^2$ であった。

#### 【0183】(4) 膜-電極複合体(MEA)の作成

前記(3)で作成した触媒層2枚と、電極基材として撥水処理を行った炭素繊維紡績糸織物(E-TEK社製ELAT、PFAの付き量25%)2枚、プロトン交換膜としてDuPont社製Nafion112を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス(温度 $130^\circ\text{C}$ 、圧力 $50\text{MPa}$ )を行うことで膜-電極複合体を作成した。

#### 【0184】(5) 燃料電池評価

前記(4)で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度； $80^\circ\text{C}$ 、燃料ガス；水素、酸化ガス；空気、ガス利用率；アノード70%/カソード40%において電流-電圧(I-V)測定を行ったところ、最高出力は、 $700\text{mW}/\text{cm}^2$ であった。

#### 【0185】実施例12

##### (1) 非導電性布帛の作成

PTFE繊維(東レ製トヨフロン)を3mmに裁断した。この3mmに裁断した短繊維PTFE繊維の半分量を取り、これを磨り潰すことによってフィブリル化した叩解PTFEを得た。3mmの短繊維PTFEを叩解PTFEをCMC水溶液に分散させ、この分散液を金網上に抄紙することによりPTFE抄紙シートを作成した。

【0186】次に、この抄紙シートを、 $370^\circ\text{C}$ で3時間熱処理後に、延伸を行いPTFEからなる非導電性布帛を作成した。この非導電性布帛の目付は $10\text{g}/\text{m}^2$ 、厚さは $10\mu\text{m}$ であった。

##### 【0187】(2) 触媒-ポリマ複合体の作成

市販のAldrich社製Nafion溶液(5重量%)5gに触媒担持カーボン(触媒；Pt、カーボン；Cabot社製VulcanXC-72、白金担持量；50wt%) $0.63\text{g}$ を良く攪拌して触媒-ポリマ複合体を含む分散液を調製した。

##### 【0188】(3) 触媒層の作成

前記(1)で作成した多孔質導電シート上に前記(2)で作成した触媒-ポリマ複合体を含む分散液をスクリーン印刷にて塗工後、乾燥させて、多孔質導電シートと触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み $20\mu\text{m}$ 、白金の付き量； $0.4\text{mg}/\text{cm}^2$ 、Nafionの付き量； $0.32\text{mg}/\text{cm}^2$ であった。

##### 【0189】(4) 電極基材の作成

長さ12mmにカットされたPAN系炭素繊維の短繊維

と膨張黒鉛粉末(東洋炭素(株)製、かさ密度 $0.14\text{g}/\text{cm}^3$ 、平均粒径 $100$ 乃至 $200\mu\text{m}$ )を、重量比で1:1に混合し、ナトリウムカルボキシメチルセルロース水溶液中に分散した。この分散液を用い、炭素繊維の短繊維に膨張黒鉛粉末が付着したシートを金網上に抄造した。水分を除去する目的で、シートを2枚の濾紙に挟み軽く加圧した。その後、濾紙を外してシートを乾燥した。乾燥後、シートをロールプレスし、多孔質導電シートを製造した。得られたシートは $80\text{g}/\text{m}^2$ であった。この多孔質導電シートを空气中で $200^\circ\text{C}$ 、30分の熱処理を行った後、PFAディスパージョン(ネオフロンPFAディスパージョン、ダイキン工業株式会社製)を含浸し、2枚の濾紙に挟んで軽く加圧、乾燥した。さらにこのシートを、 $14.7\text{kPa}$ ( $0.15\text{kgf}/\text{cm}^2$ )で加圧しながら $400^\circ\text{C}$ 、3時間の熱処理を行い、電極基材を製造した。PFAの付き量は15重量%であった。

【0190】(5) 膜-電極複合体(MEA)の作成  
前記(3)で作成した触媒層2枚、前記(4)で作成した電極基材2枚、プロトン交換膜としてDuPont社製Nafion112を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス(温度 $130^\circ\text{C}$ 、圧力 $50\text{MPa}$ )を行うことで膜-電極複合体を作成した。

##### 【0191】(6) 燃料電池評価

前記(5)で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度； $70^\circ\text{C}$ 、燃料ガス；水素、酸化ガス；空気、ガス利用率；アノード70%/カソード40%において電流-電圧(I-V)測定を行ったところ、最高出力は、 $500\text{mW}/\text{cm}^2$ であった。

#### 【0192】実施例13

##### (1) 非導電性布帛の作成

PAN系耐炎化糸を短繊維にカットしてカード化した後、ウォータージェットパンチング法にて不織布加工した。この耐炎化不織布の目付は $10\text{g}/\text{m}^2$ 、厚さは $20\mu\text{m}$ であった。

##### 【0193】(2) 触媒-ポリマ複合体の作成

市販のAldrich社製Nafion溶液(5重量%)5gに触媒担持カーボン(触媒；Pt、カーボン；Cabot社製VulcanXC-72、白金担持量；50wt%) $0.83\text{g}$ を加えて良く攪拌して触媒-ポリマ複合体を含む分散液を調製した。

##### 【0194】(3) 触媒層の作成

前記(1)で作成した多孔質導電シート上に前記(2)で作成した触媒-ポリマ複合体を含む分散液をスクリーン印刷にて塗工、乾燥後に、ロールプレスにより加圧処理を行い、非導電性布帛と触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み $10\mu\text{m}$ 、白金の付き量； $0.4\text{mg}/$



$\text{cm}^2$ 、Nafionの付き量； $0.24\text{mg}/\text{cm}^2$ であった。

【0195】(4) 膜-電極複合体 (MEA) の作成  
前記 (3) で作成した触媒層 2 枚と、電極基材として撥水処理を行った炭素繊維ペーパー (東レ製 TGP-H-060) 2 枚、プロトン交換膜として Du Pont 社製 Nafion 112 を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス (温度  $130^\circ\text{C}$ 、圧力  $50\text{MPa}$ ) を行うことで膜-電極複合体を作成した。

#### 【0196】(5) 燃料電池評価

前記 (4) で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度； $80^\circ\text{C}$ 、燃料ガス；水素、酸化ガス；空気、ガス利用率；アノード  $70\%$ /カソード  $40\%$  において電流-電圧 (I-V) 測定を行ったところ、最高出力は、 $600\text{mW}/\text{cm}^2$  であった。

#### 【0197】実施例 14

##### (1) 非導電性布帛の作成

PTFE 抄紙体 (巴川製紙製 トミーファイレック FP-50) を延伸し、目付は  $5\text{g}/\text{m}^2$ 、厚さは  $15\mu\text{m}$  の非導電性布帛を作成した。

##### 【0198】(2) 触媒-ポリマ複合体の作成

PTFE ディスパーション (ダイキン工業社製 ポリフロン TFE ディスパーション) に触媒担持カーボン (触媒；Pt、カーボン；Cabot 社製 Vulcan XC-72、白金担持量； $50\text{wt}\%$ ) を加えてよく攪拌して触媒-ポリマ複合体を含む分散液を調製した。

##### 【0199】(3) 触媒層の作成

前記 (1) で作成した非導電性布帛を前記 (2) で作成した触媒-ポリマ複合体を含む分散液に含浸後、乾燥させて、非導電性布帛と触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層を市販の Aldrich 社製 Nafion 溶液 (5 重量%) に含浸、乾燥してプロトン交換ポリマを含む触媒層を作成した。この触媒層は厚み  $15\mu\text{m}$ 、白金の付き量； $0.4\text{mg}/\text{cm}^2$ 、Nafion の付き量； $0.2\text{mg}/\text{cm}^2$  であった。

【0200】(4) 膜-電極複合体 (MEA) の作成  
前記 (3) で作成した触媒層 2 枚と、電極基材として撥水処理を行った炭素繊維紡績糸織物 (E-TEK 社製 ELAT) 2 枚、プロトン交換膜として Du Pont 社製 Nafion 112 を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス (温度  $130^\circ\text{C}$ 、圧力  $50\text{MPa}$ ) を行うことで膜-電極複合体を作成した。

##### 【0201】(5) 燃料電池評価

前記 (4) で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度； $70^\circ\text{C}$ 、燃料ガス；水素、酸化ガス；

空気、ガス利用率；アノード  $70\%$ /カソード  $40\%$  において電流-電圧 (I-V) 測定を行ったところ、最高出力は、 $600\text{mW}/\text{cm}^2$  であった。

#### 【0202】実施例 15

##### (1) 非導電性布帛の作成

PAN 系耐炎化糸を  $3\text{mm}$  に裁断した。この  $3\text{mm}$  に裁断した耐炎化短繊維を PFA ディスパーション (ネオフロン ディスパーション、ダイキン工業株式会社製) に分散させた。この分散液を金網上に抄紙することにより耐炎化繊維抄紙シートを作成した。

【0203】次に、この抄紙シートを、 $370^\circ\text{C}$  で 3 時間熱処理後に、ロールプレスを行い耐炎化短繊維からなる非導電性布帛を作成した。この非導電性布帛の目付は  $10\text{g}/\text{m}^2$ 、厚さは  $10\mu\text{m}$  であった。

【0204】この布帛をカーボンブラック (アセチレンブラック；電気化学工業社製 デンカブラック) を分散した PVDF の N-メチルピロリドン溶液に含浸し、直ちにメタノールに浸漬することにより湿式凝固を行った。これを乾燥し、カーボンブラックが 5 重量%、PVDF が 1 重量% 付着した PAN 系炭素短繊維不織布からなる多孔質導電シートを作成した。この多孔質導電シートの目付は  $4\text{g}/\text{m}^2$ 、厚さは  $20\mu\text{m}$  であった。

##### 【0205】(2) 触媒-ポリマ複合体の作成

市販の Aldrich 社製 Nafion 溶液 (5 重量%)  $5\text{g}$  に触媒担持カーボン (触媒；Pt、カーボン；Cabot 社製 Black Pearls、白金担持量； $30\text{wt}\%$ )  $1.0\text{g}$  を加えてよく攪拌して触媒-ポリマ複合体を含む分散液を調製した。

##### 【0206】(3) 触媒層の作成

前記 (1) で作成した非導電性布帛を前記 (2) で作成した触媒-ポリマ複合体を含む分散液に含浸後、乾燥させて、非導電性布帛と触媒-ポリマ複合体が一体構造となった、自立可能なシートの触媒層を作成した。この触媒層は厚み  $25\mu\text{m}$ 、白金の付き量； $0.4\text{mg}/\text{cm}^2$ 、Nafion の付き量； $0.32\text{mg}/\text{cm}^2$  であった。

【0207】(4) 膜-電極複合体 (MEA) の作成  
前記 (3) で作成した触媒層 2 枚と、電極基材として撥水処理を行った炭素繊維ペーパー (東レ製 TGP-H-060) 2 枚、プロトン交換膜として Du Pont 社製 Nafion 112 を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス (温度  $130^\circ\text{C}$ 、圧力  $50\text{MPa}$ ) を行うことで膜-電極複合体を作成した。

##### 【0208】(5) 燃料電池評価

前記 (4) で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度； $70^\circ\text{C}$ 、燃料ガス；水素、酸化ガス；空気、ガス利用率；アノード  $70\%$ /カソード  $40\%$  において電流-電圧 (I-V) 測定を行ったところ、最高

出力は、600mW/cm<sup>2</sup>であった。

#### 【0209】実施例16

##### (1) 非導電性布帛の作成

PTFE繊維（東レ製トヨフロン）を3mmに裁断した。この3mmに裁断したPTFE短繊維の半分量を磨り潰してフィブリル化し、叩解PTFE繊維を得た。3mmに裁断した短繊維PTFEと叩解PTFE繊維とをCMC水溶液に分散させた。この分散液を金網上に抄紙することによりPTFE繊維抄紙体を作成した。

【0210】次に、この抄紙体を、370℃で3時間熱処理後に延伸を行い、目付は10g/m<sup>2</sup>、厚さは10μmの非導電性布帛を作成した。

【0211】(2) 触媒-ポリマ複合体の作成  
市販のAldrich社製Nafion溶液（5重量%）を濃縮し、15重量%とした。この溶液5gに触媒担持カーボン（触媒；Pt、カーボン；Cabot社製VulcanXC-72、白金担持量；50wt%）1.88gを加えて良く攪拌して触媒-ポリマ複合体を含む分散液を調製した。

【0212】(3) 触媒層の作成  
前記(1)で作成した非導電性布帛を前記(2)で作成した触媒-ポリマ複合体を含む分散液に含浸後、直ちにメタノールに含浸して湿式凝固を行い、乾燥させ、非導電性布帛と触媒-ポリマ複合体が一体構造となり微多孔質構造を有する自立可能なシートの触媒層を作成した。この触媒層は厚み25μm、白金の付き量；0.3mg/cm<sup>2</sup>、Nafionの付き量；0.24mg/cm<sup>2</sup>であった。

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【0213】(4) 膜-電極複合体(MEA)の作成  
前記(3)で作成した触媒層2枚と、電極基材として撥水処理を行った炭素繊維ペーパー（東レ製TGPH-060）2枚、プロトン交換膜としてDu Pont社製Nafion112を用意した。電極基材/触媒層/プロトン交換膜/触媒層/電極基材をこの順で積層し、熱プレス（温度130℃、圧力50MPa）を行うことで膜-電極複合体を作成した。

##### 【0214】(5) 燃料電池評価

前記(4)で作成した膜-電極複合体をセパレータに挟み固体高分子型燃料電池セルを作成した。この燃料電池セルをセル温度；80℃、燃料ガス；水素、酸化ガス；空気、ガス利用率；アノード70%/カソード40%において電流-電圧(I-V)測定を行ったところ、最高出力は、700mW/cm<sup>2</sup>であった。

##### 【0215】

【発明の効果】本発明の触媒層により、多孔質基材上への塗布における触媒浸み込みの問題を解消し、またプロトン交換膜への塗布における膜の膨潤を回避するための煩雑な操作の問題を解消した電極が得られ、したがって、触媒の利用効率が向上し、高出力性能でかつ触媒量低減による低コスト化電極が得られる。

【0216】本発明の電極は、膜-電極複合体(MEA)に適用されるほか、通常の電気化学装置、特に固体高分子型燃料電池にも適用され、この燃料電池を用いた移動体や自動車にも適用されるものである。

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